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REGENERATION OF SPENT GRANULAR ACTIVATED CARBON

ADVANCED WASTE TREATMENT RESEARCH LABORATORY -VII

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27 Abstract

The regeneration of spent granular activated carbon, used in tertiary treatment of municipal waste water, is a three-step process, (1) drying, (2) baking and (3) activating. Laboratory studies with an indirect heated rotary tube furnace demonstrated that the rates at which the drying and baking steps are performed do not have a significant effect on the properties of the baked carbon. The controlling step for the regeneration product is the activation, and the important parameters are the carbon temperature, length of activating time, and steam or carbon dioxide concentration in the activating gas mixture. In multiple hearth furnace regenerations, where the reported carbon losses are 5% to 7% per regeneration, the characteristics of the activating step are: (1) high activating gas input rate, (2) relative short activating time, and (3) relatively low carbon temperature. Thermodynamic calculations made on the hearth furnace regeneration indicate that, by performing only the activation of a previously baked carbon, the hearth furnace gas input rate can be reduced drastically and to the point where it approaches the optimum rate of the rotary tube.

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Abstractor
George Knapp 3-5-70

Institution
U. S. Geological Survey, Water Resources Div.

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LABORATORY INVESTIGATION OF THE REGENERATION OF SPENT GRANULAR ACTIVATED CARBON

by

A. J. Juhola and F. Tepper

for

The Advanced Waste Treatment Research Laboratory
Robert A. Taft Water Research Center

This report is submitted in fulfillment of Contract No. 14-12-107 between the Federal Water Pollution Control Administration and the MSA Research Corporation.

U. S. Department of the Interior
Federal Water Pollution Control Administration
Cincinnati, Ohio

February, 1969

FOREWORD

In its assigned function as the Nation's principal natural resource agency, the United States Department of the Interior bears a special obligation to ensure that our expendable resources are conserved, that renewable resources are managed to produce optimum yields, and that all resources contribute their full measure to the progress, prosperity and security of America--now and in the future.

This series of reports has been established to present the results of intramural and contract research carried out under the guidance of the technical staff of the FWPCA's Robert A. Taft Water Research Center for the purpose of developing new or improved wastewater treatment methods. Included is work conducted under cooperative and contractual agreements with Federal, state, and local agencies, research institutions, and industrial organizations. The reports are published essentially as submitted by the investigators. The ideas and conclusions presented are, therefore, those of the investigators and not necessarily those of the FWPCA.

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ABSTRACT

The regeneration of spent granular activated carbon, used in tertiary treatment of municipal waste water, is a three-step process, (1) drying, (2) baking and (3) activating. Wet, drained carbon, as received from the drain bin, is dewatered in the drying step at carbon temperatures in the range 60°F to 212°F. During the baking step, the organic adsorbate is carbonized, accompanied by evolution of gases and a formation of free carbon residue in the micropores of the activated carbon. This occurs in the temperature range 212°F to 1500°F. In the activating step, the goal is to oxidize the carbon residue with minimum damage to the basic pore structure and thereby restore the original properties of the virgin carbon. In multiple hearth furnace regenerations, the activation occurs at an activating gas temperature of 1700°F and carbon temperatures in the range 1500°F to 1650°F. The activating gas is flue gas with varying amounts of additional steam.

Laboratory studies with an indirect heated rotary tube furnace demonstrated that the rates at which the drying and baking steps are performed do not have a significant effect on the properties of the baked carbon. The controlling step for the regeneration product is the activation, and the important parameters are the carbon temperature, length of activating time, and steam or CO_2 concentration in the activating gas mixture.

In multiple hearth furnace regenerations, where the reported carbon losses are 5 to 7% per regeneration, the characteristics of the activating step are: (1) high activating gas input rate, (2) relative short activating time, and (3) relatively low carbon temperature. Operation of the hearth furnace requires a high activating gas input rate because it is direct-fired and because of the high heat requirement for the drying and baking steps. In the laboratory investigations, a set of operating conditions were found with the rotary tube regenerator, whereby the regeneration losses were reduced to 2%. The characteristics of the activating step for the rotary are: (1) low activating gas input rate, (2) longer activating time, and (3) higher activating temperature. In the hearth furnace, activating rate is controlled by the carbon temperature and in the rotary tube regenerator, by the activating gas input rate. Mean values for these parameters for the two methods of activation are:

	Rotary tube	Hearth furnace
N_2-std ft^3/lb carbon	7.4	27.3
CO_2-std ft^3/lb carbon	1.0	3.3
Steam-std ft^3/lb carbon	1.9	23.5
O_2-std ft^3/lb carbon	0.0	0.7
Activating time, min	16	11
Mean carbon temperature, °F	1630	1570
Gas utilization ($CO + H_2O$), %	83	18

Thermodynamic calculations made on the hearth furnace regeneration indicate that, by performing only the activation of a previously baked carbon, the hearth furnace gas input rate can be reduced drastically and to the point where it approaches the optimum rate of the rotary tube. Further laboratory study to determine the feasibility and economics of this procedure is recommended.

INTRODUCTION

The purpose of the work reported herein was to gain general knowledge of the regeneration process and to determine the optimum regenerating conditions. Since the direct-fired multiple hearth furnace is, at present, the most widely used, the laboratory work was oriented to permit translation of laboratory results to hearth furnace operations. Construction of a miniature multiple hearth furnace was not feasible. In any event, the versatility of such a miniature furnace for parametric studies would be limited by the direct firing feature. A continuous-feed, externally-heated, rotary tube regenerator, which met the requirements of the study, was constructed and used. This device permitted independent control of most of the parameters and, at the same time, permitted operation at conditions close to those used in the multiple hearth furnace.

The work described herein was conducted in cooperation with the Pomona Water Reclamation Plant, Pomona, California. (The Pomona pilot plant study is a joint project of the Federal Water Pollution Control Administration and the Los Angeles County Sanitation District.) For the laboratory studies, various quantities of virgin carbon and carbons that had been spent and regenerated were received from Pomona. The virgin carbon used at Pomona is the Pittsburgh Carbon Company Filtrasorb 400, a 12x40 mesh coal-based carbon. The spent carbons were: (1) I7A, spent eight times and regenerated seven, (2) V1A, spent twice and regenerated once, and (3) once-spent, virgin Filtrasorb 400. Operating data received from Pomona on the multiple hearth furnace permitted thermodynamic calculations and a closer study of the furnace operating conditions.

In the beginning of the experimental studies, it was recognized that the regeneration process would involve two steps: (1) that of drying, since the carbon as received from the contactors is wet and (2) the activation by steam, CO_2 and possibly O_2. Because of the high heat of vaporization of water, the carbon temperature was expected to remain near 212°F until most of the water was driven off. At this temperature no other activity was expected to occur.

Early in the study, it became evident that another step occurred immediately following the drying step and before the activating step. In this step, called the baking step, the adsorbate is carbonized in such a manner that part of it is evolved as gases and the rest broken down to free carbon. This process occurs in the 212°F to 1500°F temperature range. The regeneration was then broken down to three steps; (1) drying, (2) baking and (3) activating. These steps were then studied individually as unit operations to determine their effect on the overall regeneration.

The degree of success in the three regenerating steps was determined by five measurements, namely:

1. Bulk volume
2. Particle volume
3. Real density or volume of nonporous carbon
4. Iodine number
5. Molasses number

SUMMARY

Adsorption by granular activated carbon is among the most promising advanced waste treatment processes for tertiary treatment of sanitary waste water. Its acceptance depends on an economical regeneration of the carbon to permit its reuse over many adsorption-regeneration cycles. At present, a 2.5 MGD facility is in operation at South Lake Tahoe, California and a 0.3 MGD pilot unit is under study at Pomona, California. A large-scale facility is in operation at Nitro, West Virginia to purify river water for domestic use. At each of these facilities, the regeneration is accomplished in a direct-fired multiple hearth furnace. The combustion of natural gas with air is used as the heat source while carbon dioxide, oxygen and steam, as part of the combustion products, are the activating agents. Generally, extra steam is added at a rate of one pound per pound of regenerated product.

Carbon losses of 5% during each adsorption-regeneration cycle have been reported at Tahoe and Nitro and 7% at Pomona. It is highly desirable to reduce these losses since the cost of the make-up carbon is a large portion of the regeneration cost. According to estimates made at the Pomona Water Reclamation Plant, the overall cost of the treatment with carbon is 8.3¢/1000 gal. of water, of which 1.1¢ is carbon make-up cost when carbon losses are 10% in an adsorption-regeneration cycle.

The work reported herein consisted of laboratory studies to gain general knowledge of the regeneration process and to determine the optimum regeneration conditions for carbon spent in tertiary treatment of waste water. The regenerations were accomplished in an externally-heated rotating tube regenerator with activating gas and carbon contacted in a continuous counter-current flow pattern. The regenerator was designed to allow maximum solid recovery, permitting accurate mass balances to be performed. The mechanical attrition (physical loss under nonregenerating conditions) in the regenerator is less than 0.2%. The design permits alteration of both carbon feed rate and degree of mixing of the granules with the regenerating or activating gas. The activating gas consisted of nitrogen, carbon dioxide and steam in the proportions found in flue gas. Excess steam was also used. The degree of carbon loss was computed from weight, bulk and particle volume changes and the degree of adsorptive capacity recovery was determined by the decolorizing tests, iodine number and molasses number.

The studies demonstrated that the carbon regeneration is a three-step process: (1) drying, (2) baking (pyrolysis of adsorbates) and (3) activating (oxidation of the carbon residue from the decomposed adsorbate). The drying occurs predominantly in the room temperature to 212°F range, the baking from 212°F to 1500°F and activating at temperatures above 1500°F. These are naturally-occurring steps that also characterize the multiple hearth regeneration. With Pomona six-hearth furnace operating data and knowledge obtained from the laboratory studies, thermodynamic calculations were made on the Pomona furnace operations. A computed carbon temperature profile for the furnace clearly defined the three steps, with the drying occurring on the first three hearths, baking on the fourth and activating on the fifth and sixth.

The studies carried out on the three steps of the regeneration process showed that the manner in which the drying and baking are carried out has no significant effect on the properties of the baked carbon. Length of baking time was varied from 4 minutes to 6 hours with slow rise in temperatures and with a fast rise in temperature, in all cases to 1500°F and higher. The bulk density of the baked product was always the same within narrow limits. In every case, the nonvolatile portion of the adsorbate was reduced to essentially free carbon as determined by the real density measurements. Carbons baked under a variety of conditions, when subsequently activated under identical conditions produced final products of nearly identical properties. Results of these studies showed that the carbon dyring and baking conditions were also not decisive factors in the quality of the product from the multiple hearth furnace.

Laboratory regeneration studies produced a set of activating conditions which essentially recovered the physical properties of the virgin carbon with a carbon loss of about 2.0%. The activating conditions were characterized by a low gas input per pound of regenerated carbon, an activating time of 16 minutes, and a relatively high activating temperature of 1630°F. Under these conditions, the activating gas utilization was 83%. In contrast, the activating conditions in the multiple hearth furnace are characterized by a high gas input rate, an activating time of 11 minutes, and a lower activating temperature of about 1570°F. The gas utilization in the multiple hearth furnace was about 18%. In the rotary tube, the oxidative controlling parameter is the activating gas input rate, while in the hearth furnace, the controlling parameter is the carbon temperature. The experimental evidence obtained indicates that the high activating gas input rate is the cause of the higher carbon losses in the hearth furnace regeneration.

Mean values of these parameters for the two methods of activation are given below. The gas input is per lb of regenerated carbon.

	Rotary tube	Hearth furnace
N_2-std ft^3/lb carbon	7.4	27.3
CO_2-std ft^3/lb carbon	1.0	3.3
Steam-std ft^3/lb carbon	1.9	23.5
O_2-std ft^3/lb carbon	0.0	0.7
Activating time, min	16	11
Mean gas temperature, °F	1670	1700
Mean carbon temperature, °F	1630	1570
Gas utilization ($CO + H_2O$), %	83	18

The carbon activated in the rotary tube is once-spent Filtrasorb 400 and was regenerated to the initial virgin carbon properties. The physical properties of this carbon, activated in the rotary tube, are given below. The data shows the progression through the three steps of the regeneration. For comparison, the properties of the initial virgin Filtrasorb 400 are also given.

	Dried Spent	Baked	Activated	Virgin Filtrasorb 400
Bulk density, g/cc	0.584	0.532	0.502	0.490
Particle density,g/cc	0.971	0.871	0.825	0.810
Real density, g/cc	1.88	2.07	2.13	2.15
Pore volume,cc/cc p.v.*	0.483	0.578	0.612	0.618
Iodine number	673	955	1017	1010
Molasses number	174	193	192	200

*p.v. = particle volume

When the drying and baking functions are eliminated from the hearth furnace regeneration (i.e., when the carbon is not placed in the regenerator until dried or baked) the computed operating conditions begin to approach those of the laboratory rotary tube activation, as shown below. The columnar captions refer to the conditions of the carbon (i.e., pretreatment) before it is charged into the activator.

	Hearth Furnace Activating Conditions	
	Dried Spent Carbon	Baked Spent Carbon
Activating time, min	15	15
Mean gas temp., °F	1700	1680
Carbon temp., °F	1500 to 1650	1500 to 1650
N_2-std ft^3/lb carbon	16.5	14.3
CO_2-std ft^3/lb carbon	2.0	1.7
Steam-std ft^3/lb carbon	14.2	12.3
O_2-std ft^3/lb carbon	0.45	0.36
Act. gas utilization, %	29.5	43.0

In the furnace activation of the baked spent carbon, about 41% of the gas-air input is required to heat the carbon to activating temperature and make up heat losses through the furnace shell; hence, the activating gas input is still larger than needed for the activation. Relative to the wet regeneration, the gas-air input rate is about 50%.

Vent gas analysis was investigated as a method for monitoring the activation. Although it offered some promise, it also posed unsolved problems.

In the hearth furnace regeneration, hot carbon is discharged into water. At the Pomona plant, this quenching action has been found to reduce the iodine number. Laboratory investigations during the present study produced a decrease in iodine number units ranging from 25 to 69 compared to 50 to 100 at Pomona.

LABORATORY REGENERATING EQUIPMENT

Rotary Tube Regenerator Unit

A continuous-feed, indirectly heated rotary tube regenerator was selected for carbon regeneration studies because it offers the widest range of versatility with respect to operating parameters. With this unit, activating gas composition and input rate can be varied to any practical limit. Heat input rate can be varied independently of the activating gas input rate and carbon residence time can be varied independently of other parameters.

Figure 1 shows the side view of the unit with some of the essential components indicated by callouts. These callouts, further identified by letters, are explained in more detail below.

a. Furnace - electrically heated, three heating sections.

b. Rotating tube.

c. Volumetric Feeder - acrison, auger type, (feed range 0.010 to about 0.10 ft^3 carbon/hr, feeds carbon through 1/2 inch tubing to rotary tube).

d. Steam Generator - electrically heated with calibrated sight glass.

e. Heated vent line.

f. Motor - Bodine variable speed drive for tube, (tube rotation range 0 to 2.4 rpm).

Figure 2 shows additional components of the regenerative unit.

g. Superheater - gas burner heated for the N_2, CO_2 steam mixture.

h. Product Receiver - two quart Mason jar.

i. Water Manometer - indicates pressure in unit, normal pressure less than 5 mm.

Figure 3 shows the temperature control and vent gas monitoring instruments. Letters j, k and l respectively denote

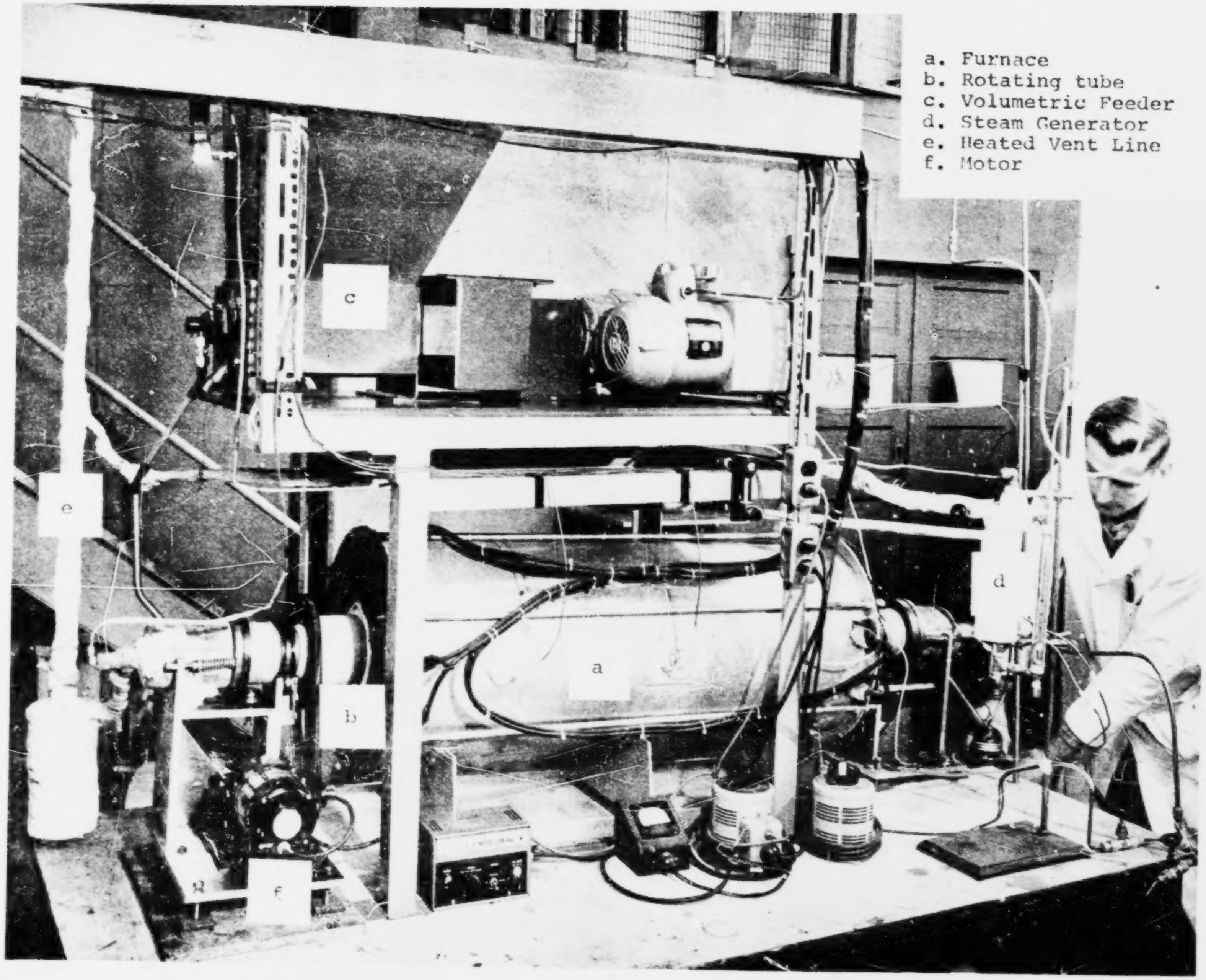


FIGURE 1 - ROTARY TUBE REGENERATOR, SIDE VIEW

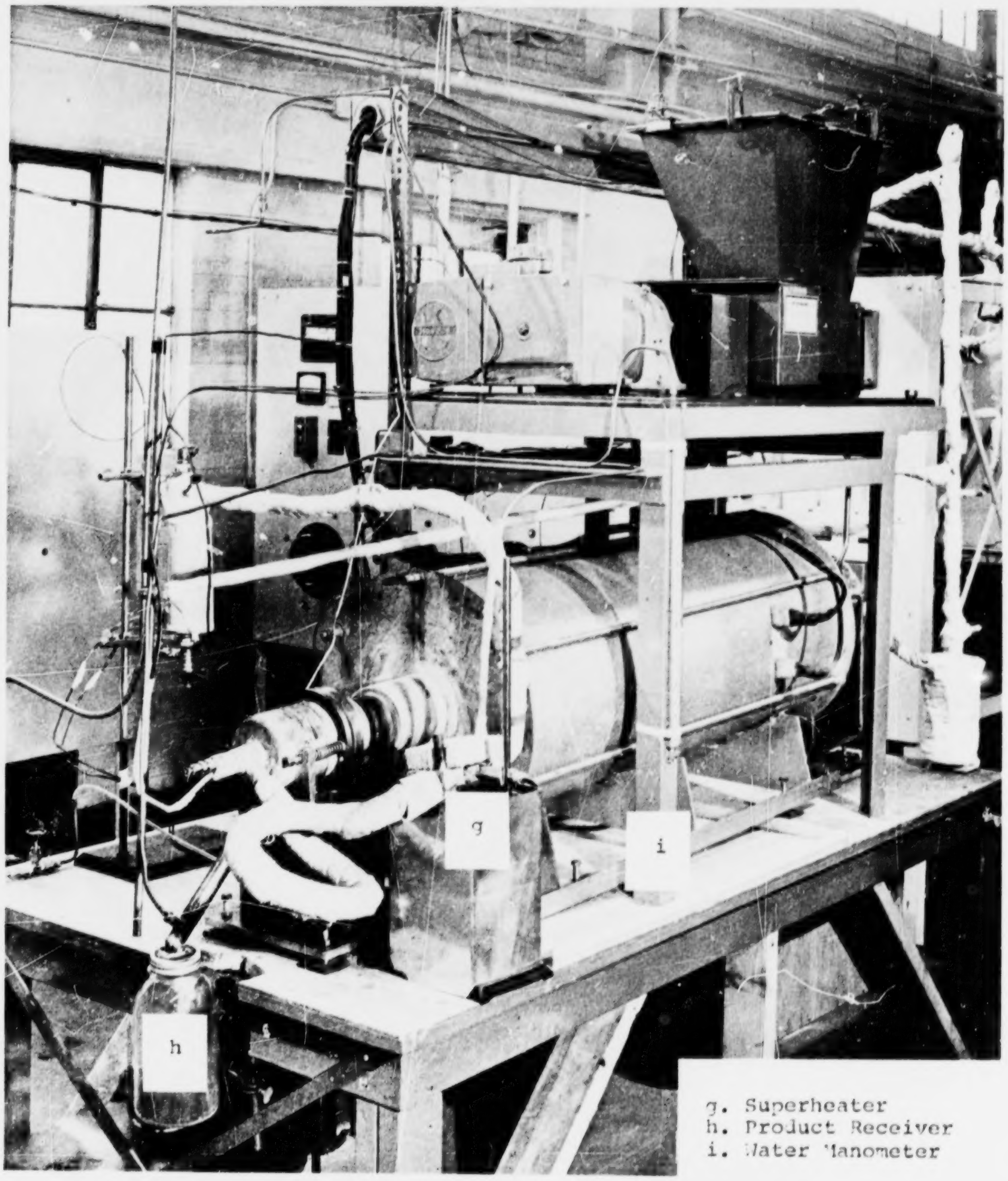
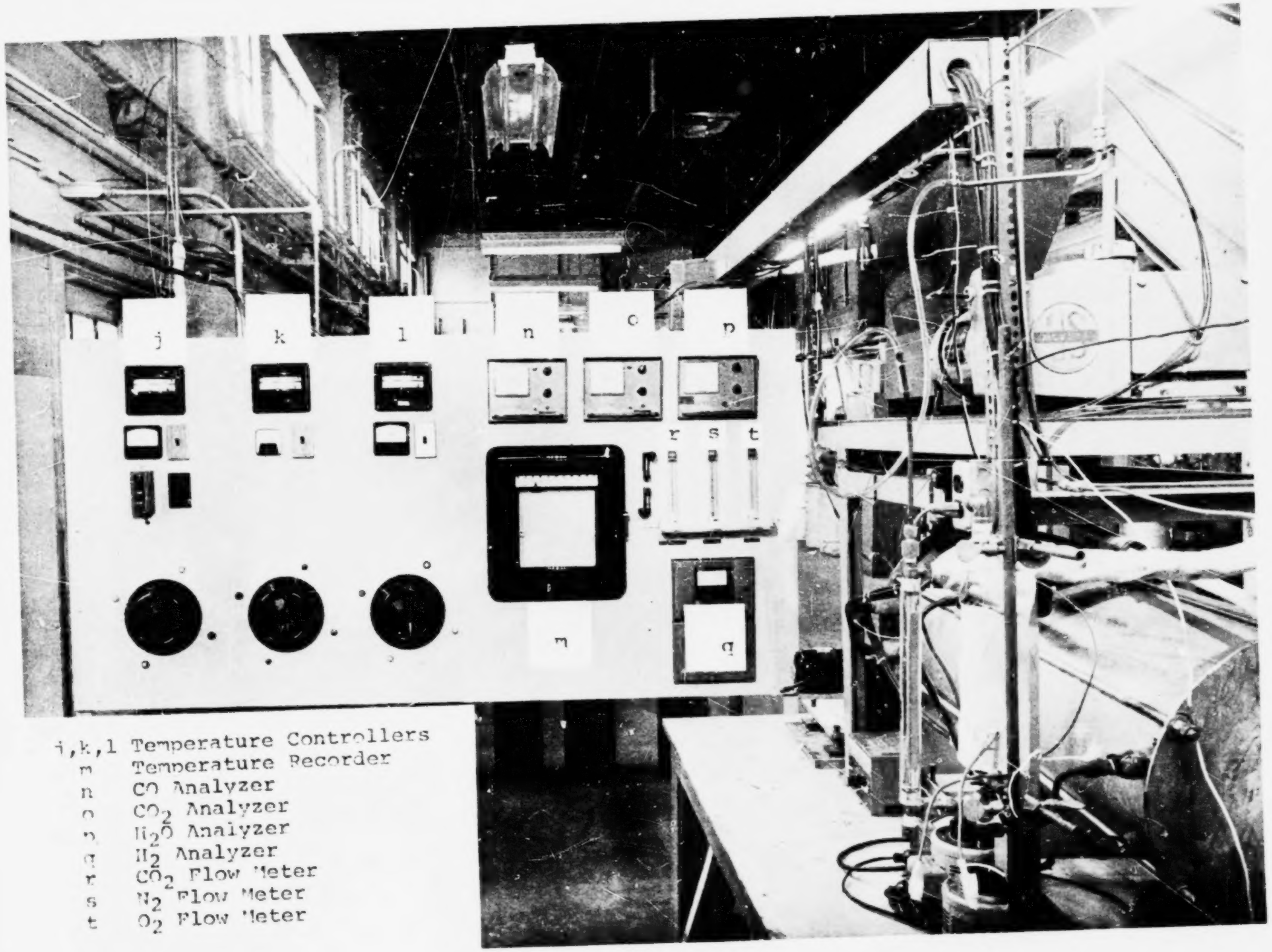


FIGURE 2 - ROTARY TUBE REGENERATOR, END VIEW



j,k,l	Temperature Controllers
m	Temperature Recorder
n	CO Analyzer
o	CO_2 Analyzer
p	H_2O Analyzer
q	H_2 Analyzer
r	CO_2 Flow Meter
s	N_2 Flow Meter
t	O_2 Flow Meter

FIGURE 3 - OPERATING CONTROL PANEL FOR ROTARY TUBE REGENERATOR

West temperature controllers, ammeters and variable transformers to control the temperatures in the three sections of the furnace shown in Figure 4.

m. Temperature Recorder - twelve point Speedomax Type G. Five points are used to monitor the temperature in the rotary tube, indicated by the thermocouples TC(1), TC(2), etc.

n. CO Analyzer - Lira Model 300, 0.35% range.

o. CO_2 Analyzer - Lira Model 300, 0-15% range.

p. H_2O Analyzer - Lira Model 300, 0-35% range.

q. H_2 Analyzer - Thermatron, 0-20% range.

r. CO_2 Flow Meter - 2.1 std ft^3/hr max.

s. N_2 Flow Meter - 19.0 std ft^3/hr max.

t. O_2 Flow Meter - 4.3 std ft^3/hr max.

Figure 4 shows the cross sectional side view of the electrically heated furnace, rotary tube, sealed end caps and product receiver. The tube assembly is completely sealed to prevent any loss of gases or carbon. An accurate material balance is potentially possible although this has not been accomplished on the gas input and output.

Other pertinent details of the unit are listed below:

Tube size and material	- 3.25 in. ID x 65 in. length, 316 stainless steel
Flights	- six 1/4 in. deep flights about the full length of tube. This depth flight gives carbon a rolling action rather than a lift and free fall.
Heating	- the heated portion of tube corresponding to furnace length is 42 inches, carbon residence times are reported for the 42 inches rather than the total 65 inches.

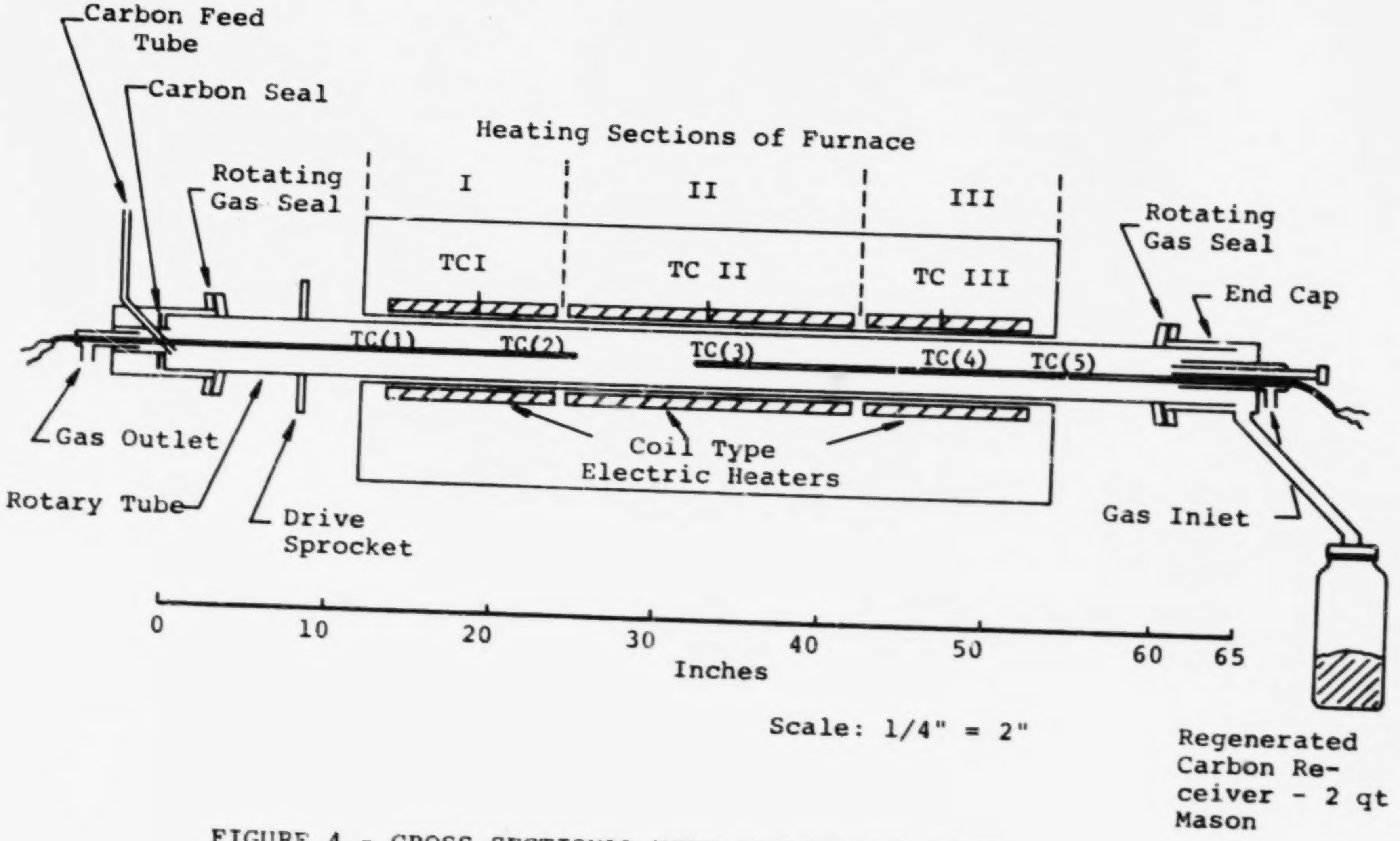


FIGURE 4 - CROSS SECTIONAL VIEW OF ROTATING TUBE, END CAPS AND HEATING FURNACE

Tube inclination - has been varied from level to 4 in. per 42 in. of tube length.

Carbon residence time - carbon residence time for 42 in. of tube length, has been varied from 10 min to 3.7 hr by varying inclination and rotation rate.

Operating Characteristics of Rotary Tube Regenerator

The rotary tube regenerator unit was sized to handle about 2300 cc bulk volume of carbon at feed rate of 0.016 ft^3/hr (450 cc/hr) in a 9-hr work period. In the baking runs, the feed time for about 2290 cc carbon was about 5 hr and in the activating runs the feed time for about 2040 cc was about 4.5 hr.

In order to maintain good operating control of the regenerator and to obtain reliable operating data, the major part of the carbon throughput must occur under steady-state conditions. The degree of steady-state operation obtained on a run depends on the residence time. For the carbon charge volumes and feed rate mentioned in the previous paragraph, the degree of steady-state operation achieved for different residence times are given below:

Residence Time	Steady-state operation as percent of total run time	
	Baking	Activating
2.0 hrs	61	56
1.5 hrs	71	67
1.0 hrs	80	78
30 min	90	89
15 min	94	94
10 min	98	98

The more important data in this study were obtained from the shorter runs of 30 min or less, where the percentages were 90 and over. The greatest deviation from steady-state operating conditions occurred at start-up when the carbon front meets the activating gases at full strength over the total tube length.

Another important parameter is the activating gas residence time. During the study, the gas residence time varied from 13 to 36 seconds, compared to only 6 seconds for hearth furnace operations. Other conditions being equal, an increased residence time increases the utilization of the activating gases, i.e.,a larger percentage of them are used.

Other operating parameters that should be recognized are listed below, although their effect on the activation process has not been determined.

Parameter	Range
carbon loading of rotary tube	1.3 to 15.8% of tube volume
carbon bed depth at maximum point	0.16 to 0.68 inches
carbon roll over rate	1.1 to 14.5 times/min

OPERATING PROCEDURE FOR ROTARY TUBE REGENERATION

Charge and Sample Preparation

The wet spent carbon received from the Pomona plant is first dried for 48 hrs at 150°C in a small air convection oven. About 3 liters of carbon, divided into four 1-liter beakers, are dried at a time. The dried spent carbon is then sieved to remove any +14 mesh aggregates and -40 mesh fines. Next, the carbon is blended to insure uniform particle size distribution throughout the charge. The blending is done by separating the carbon into an upper half fraction and a lower half fraction and then pouring the two fractions simultaneously back into a common container. This routine is repeated four times.

The charge for the baking run consists of a weighed 2450 cc of the blended carbon, with volume measured by the technique described later under test procedures. During the run, there is usually some segregation of the particles; the large particles appear to travel through the regenerator faster than the small ones. After baking,the product is then blended by the above procedure, reweighed and volume measured. Samples are taken out for various tests and 2200 cc are charged to the unit for the activation run.

The feed hopper has a space below the feeding augar where 160 to 180 cc of carbon charge remains after completion of the feeding. This carbon is removed by means of a spout at the bottom of the hopper. After removal, its volume and weight are subtracted from the volume and weight of the charge to determine the amount of carbon charge fed to the regenerator.

Control of Gas Temperature in Tube

The heating furnace consists of three sections which can be adjusted individually to maintain the gas temperature in the tube at thermcouples TC(2) , TC(3) and TC(4), shown in Figure 4, at the desired temperatures. The reported temperatures by these three thermocouples are recorded in tables under the heatings TC(2), TC(3) and TC(4).

Vent Gas Analysis

The gas analyzers for CO, CO_2 and H_2 were calibrated against standard mixtures of each gas with nitrogen before the beginning of each run. The water analyzer was not used during the program because of difficulties with its operation. One and one half cubic feet per hour of gas, dried by passing through a dry ice trap, was withdrawn from the vent line and passed through the analyzer. Based on the known nitrogen flow and percentages of CO, CO_2 and H_2, the flow rates of these three gases were then computed. A water-cooled condenser was installed on the vent line to obtain a measure of the water vapor remaining in the vent gases.

MULTIPLE HEARTH FURNACE

Figure 5 shows the essential features of the six-hearth furnace used at the Pomona Water Reclamation Plant. The furnace consists of a vertical refractory-lined cylindrical shell containing a series of horizontal hearths positioned one above the other. The wet spent carbon enters hearth number 1 at the outer edge and is then mechanically moved in a spiral pattern toward the center of hearth 1 by the rotating rabble arms. Near the center the carbon drops to hearth number 2 and is mechanically moved to the outer edge of hearth number 2 where it drops to hearth 3. In this manner, the carbon traverses each of the six hearths until delivered from discharge pipe of hearth number 6. At each of hearths 4, 5 and 6 are two gas burners and steam inlet tubes, one on each side of the cylindrical shell (not shown). The hot steam and flue gases from these burners travel upward through the hearths, countercurrent to the movement of the carbon.

A principal advantage of the multiple hearth furnace, over the direct-fired rotary type is its greater reaction surface-area-to-furnace-volume ratio, which minimizes capital costs while maximizing throughput capacity. Compared to indirect-heated rotary tube furnaces, the multiple hearth furnace has the advantage of interior construction of predominantly refractory materials. The indirect-heated unit's metal tube is more expensive and not as durable.

A primary disadvantage of any direct-fired furnace is that the heating requirement cannot be readily separated from the activating gas requirement. The ranges over which the operating parameters can be varied independently are thus greatly restricted. In carbon regeneration, this has a direct bearing on the carbon losses. In this respect the indirect-heated tube regenerator has definite advantages.

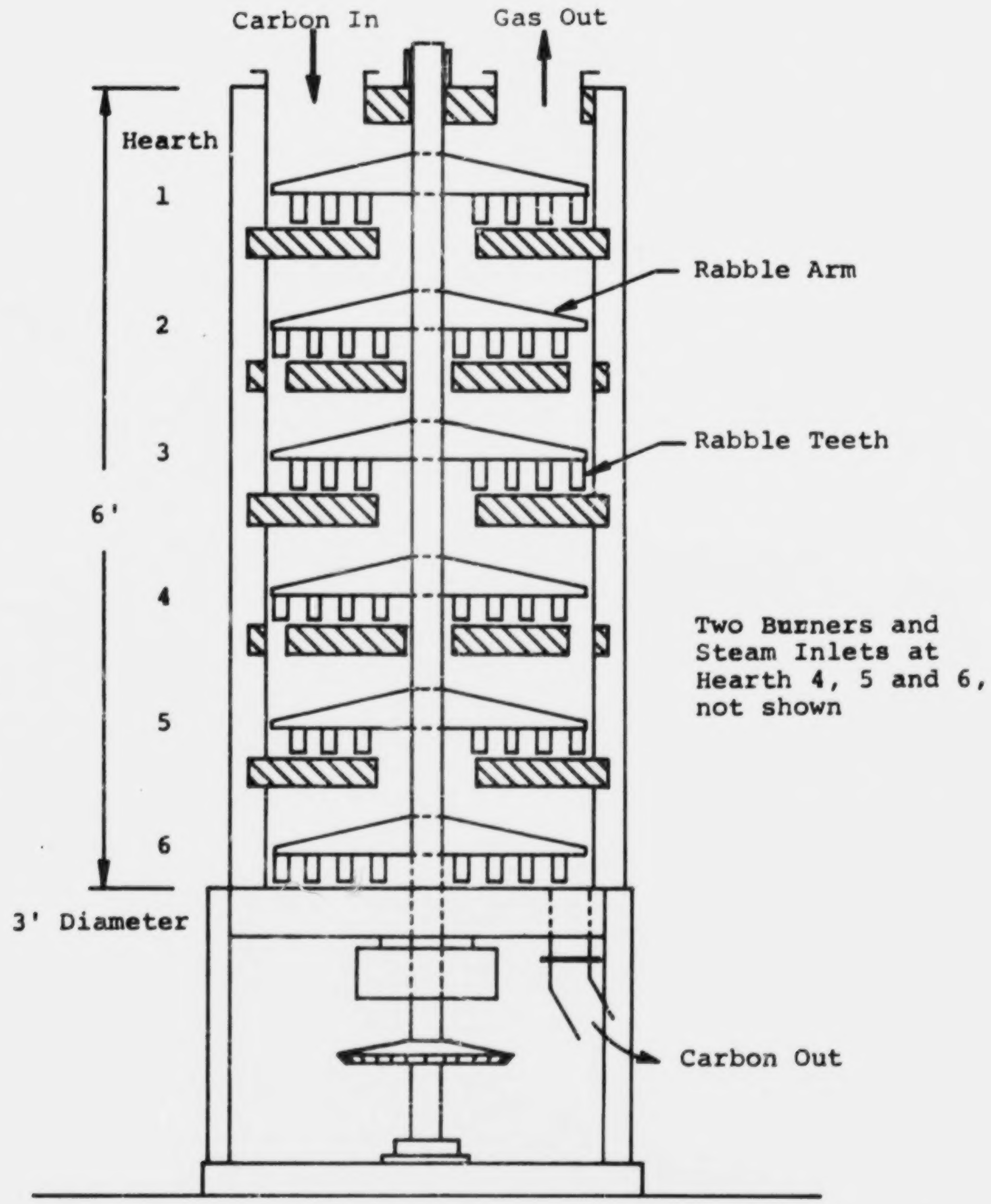


FIGURE 5 - CROSS SECTIONAL VIEW OF MULTIPLE HEARTH FURNACE USED AT POMONA WATER RECLAMATION PLANT

MULTIPLE HEARTH FURNACE REGENERATION

The three steps (drying, baking and activating) of regeneration are naturally occurring steps that also characterize the multiple hearth regeneration. With operating data from the Pomona furnace and knowledge obtained from the laboratory studies, thermodynamic calculations were made on the Pomona furnace operations. The carbon temperature profile, as given in Figure 6, represents a part of these results. As indicated in the figure, drying occurs on the first three hearths, baking on the fourth and activating on the fifth and sixth. Drying requires 15 minutes, baking 4 minutes and activating about 11 minutes. The gas temperature profile was determined by direct measurement.

For the above thermodynamic calculations, the regenerated carbon discharge rate is about 89.4 lb/hr. The recalculated wet spent carbon feed rate to the top of the regenerator is 194.0 lb/hr, of which 77.5 lb/hr is water, 13.2 lb/hr is volatiles driven off during baking, 7.6 lb/hr is adsorbate carbon residue oxidized during activation and 6.3 lb/hr is loss of basic carbon structure during activation. The 6.3 lb/hr represents the 7% carbon loss during the regeneration part of the cycle. The initial adsorbate "content" is 20.8 lb/hr, of which 13.2 lb/hr is volatilized during baking, leaving a 7.6 lb/hr free carbon residue, which is then oxidized during the activating.

In terms of heat input, the drying step consumes 40% of the heat, and the baking 8%. If the drying and baking were done outside of the hearth furnace, the heat requirement or gas-air input would be approximately 52% of the amount required for wet carbon regeneration. The excess gas-air input to carry the drying and baking functions supplies the activation step with excess activating gases such that the risk of damaging the carbon is high. In normal wet carbon regeneration, about 18% of the activating gases are utilized - about 8.5% for useful oxidation of adsorbate carbon residue (7.6 lbs/hr) and 7.0% for external oxidation of the carbon particles. On successive adsorption-regeneration cycles, the iodine number was observed to decrease from the 1097 for the virgin carbon to 655 for the regenerated carbon on the 8th cycle. Along with the 7.0% carbon volume loss, a loss of micropore volume is also occurring.

In view of the high throughput rate of activating gases, the tendency for external oxidation is greatly moderated by the short (11-minute) activating time and the relatively low (1500°F) carbon temperature.

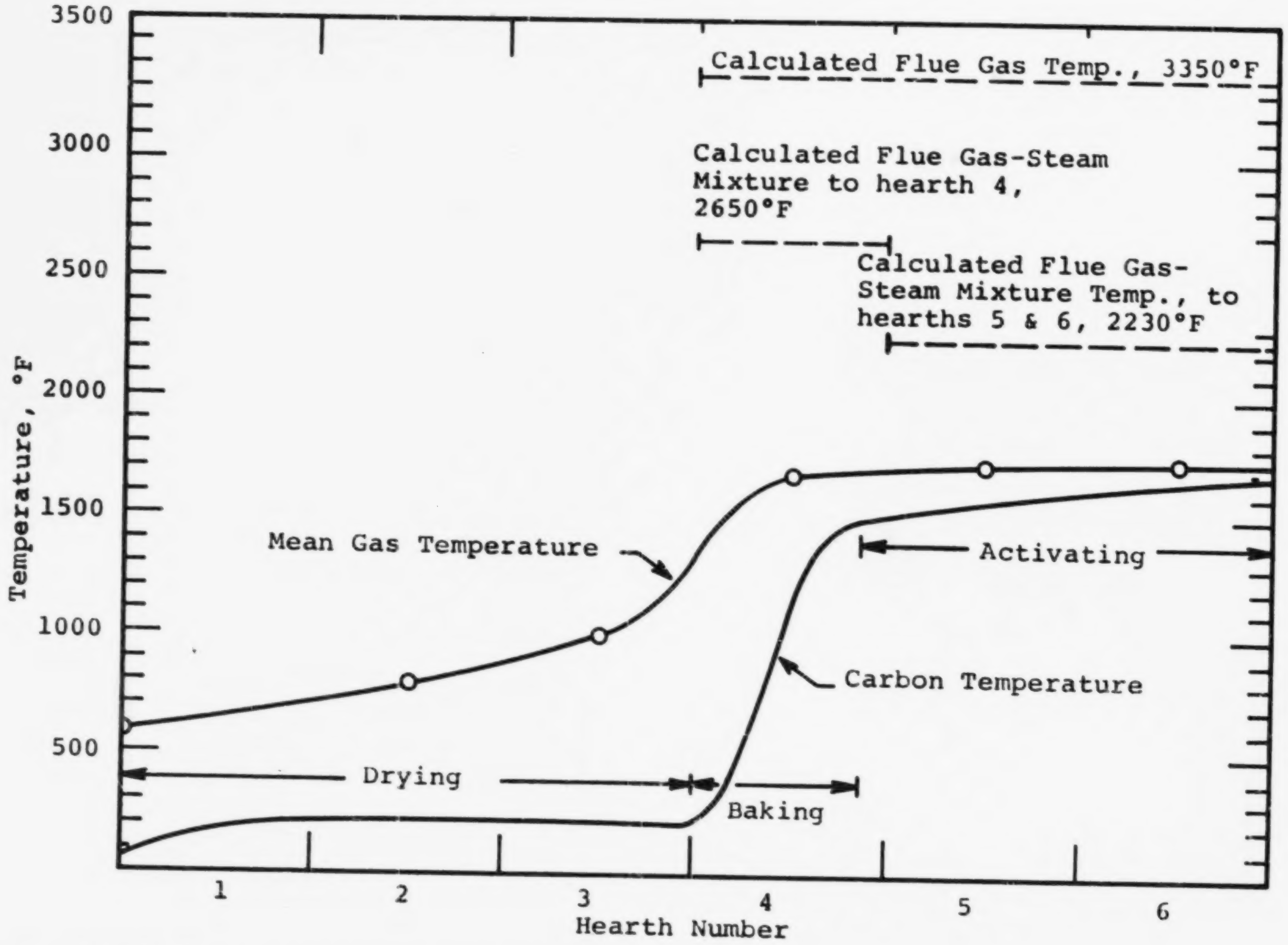


FIGURE 6 - TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE HEARTH FURNACE, REGENERATION OF WET SPENT CARBON

TEST EQUIPMENT AND PROCEDURES

Bulk Volume Measurements

The bulk volume or bulk density is a conveniently measured property of the carbon that can be used for control purposes during regeneration. The bulk density of virgin Filtrasorb 400 has been measured at 0.486, 0.495 and 0.501 g/cc, hence the goal for the regeneration is a density in this range. With experience the operating parameters can be adjusted to consistently achieve final density in this range.

A measured change in bulk volume, before and after regeneration, is a partial measure of the loss of basic carbon structure. This method is used at the Pomona Water Reclamation Plant. The contactor is initially filled to a known level; after the carbon has been spent and regenerated, it is returned to the contactor. The weight of additional carbon to fill the contactor to the initial volume represents the loss of carbon on the adsorption-regeneration cycle.

The apparatus for measuring the bulk volume, and also the bulk density, is shown in Figure 7. It consists of a funnel-hopper at the top, a one liter graduated cylinder at the lower end and a glass tube section in the middle containing 4 or 5 screens of 1/4 in. mesh. All parts of the apparatus must be aligned around the center axis and be perfectly plumb to give an even horizontal carbon surface in the graduated cylinder. The hole in the funnel is about 5/16 inches in diameter, allowing a flow rate of about 400 cc/min for a 14 to 40 mesh carbon.

The bulk volume apparatus has been found to give very reproducible results when the carbon is well mixed, i.e., is blended. Bulk volume measurements are given in Table 1 for a complete regeneration run which demonstrates the reproducibility of the measurements and the method for determining the bulk volume decrease.

The bulk volume apparatus does not give reliable measurements for volumes below 100 cc. The 30 cc on run 51 was calculated using the weight and 0.489 g/cc bulk density.

To calculate the bulk volume decrease, it is necessary to measure the carbon remaining in the feeder hopper. For run 50, it was 180 cc and for run 51, 160 cc.

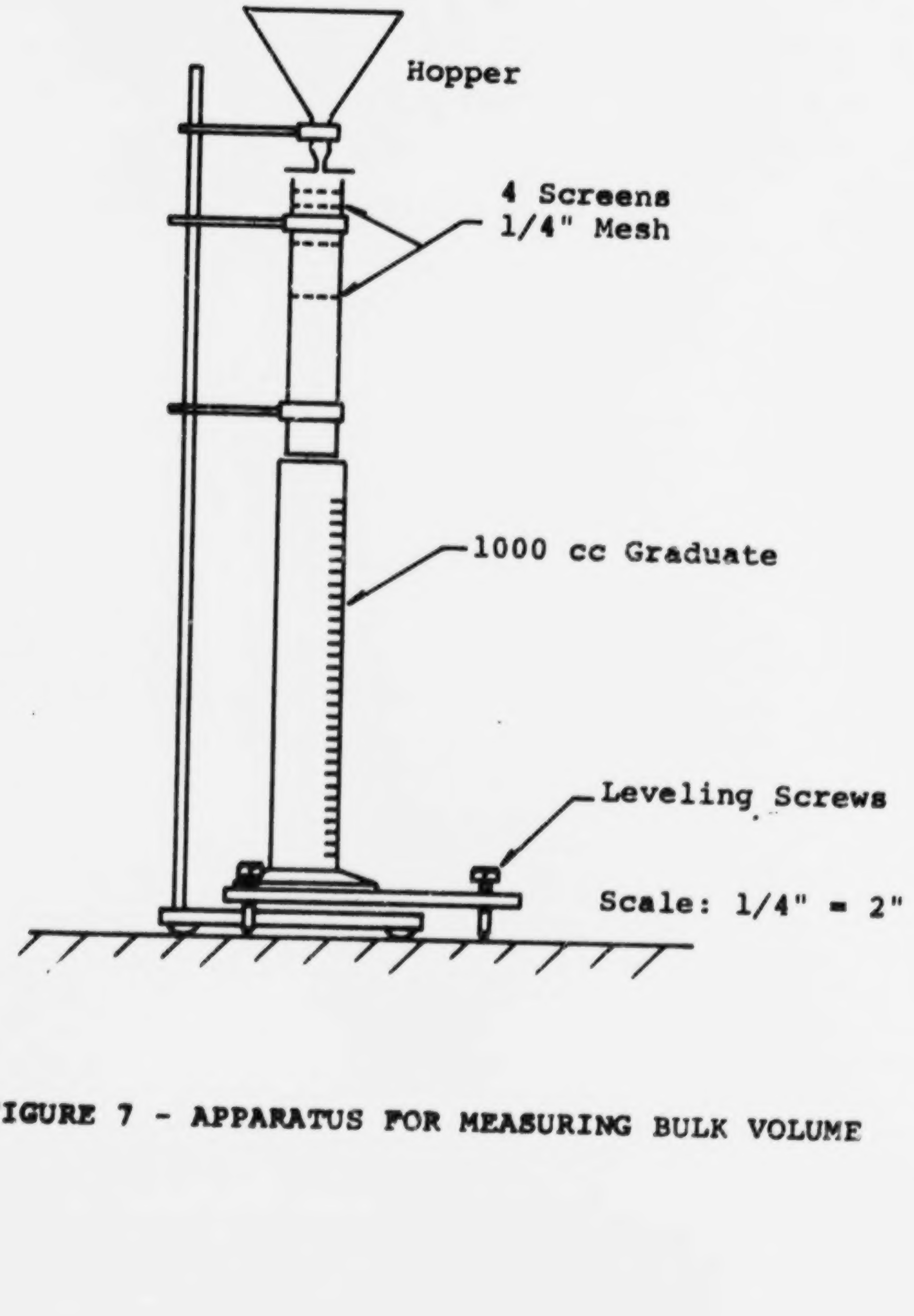


FIGURE 7 - APPARATUS FOR MEASURING BULK VOLUME

TABLE 1 - BULK VOLUME AND WEIGHT MEASUREMENTS FOR RUNS 50 AND 51

1. Feed for baking run 50
   Charged to feeder hopper, dried spent V1A carbon

Measurement No.	Bulk volume, cc	Weight, g	Density, g/cc
(1)	1000	615.5	0.615
(2)	1000	615.6	0.616
(3)	450	277.6	0.617
	2450	1408.7	mean 0.616

2. Baking run 50, product

Measurement No.	Bulk volume, cc	Weight, g	Density, g/cc
(1)	1000	548.5	0.549
(2)	1000	547.7	0.548
(3)	248	134.3	0.542
	2248	1230.5	mean 0.547

3. Activating run 51 feed
   Charged to feeder hopper, baked product run 50

Measurement No.	Bulk volume, cc	Weight, g	Density, g/cc
(1)	1000	548.5	0.549
(2)	1000	547.7	0.548
(3)	200	108.9	0.545
	2200	1205.1	mean 0.548

4. Activating run 51 product (regenerated)

Measurement No.	Bulk volume, cc	Weight, g	Density, g/cc
(1)	1000	489.4	0.489
(2)	1000	488.8	0.489
(3)	30	15.6	-----
	2030	993.8	mean 0.489

Bulk volume decrease for baking run 50

$$2450 - (180 + 2248) = 22 \text{ cc}$$

or

$$\frac{22}{2270} \quad 100 = 0.97\%$$

Bulk volume decrease for activating run 51

$$2200 - (160 + 2030) = 10 \text{ cc}$$

or

$$\frac{10}{2040} \quad 100 = 0.49\%$$

Bulk volume decrease for regeneration

$$0.97 + 0.49 = 1.46\%$$

While the above values are not truly additive from a mathematical standpoint, no significant error is being introduced.

An error can occur in measuring the carbon loss in this manner if the carbon particle size distribution changes during the regeneration. This is due to possible void space changes between the particles caused by the change in distribution of the particles. The void space may remain unchanged, increase or decrease. The bulk volume decrease may or may not be, in its entirety, a loss of carbon but also, in part, a change in void space.

Particle Volume Measurements

The particle volume measurement excludes the void space between the particles, but includes the solid carbon structure and pore volume. From the standpoint of void space change, the particle volume measurement is a more accurate method for measuring carbon loss during regeneration.

This measurement is made with mercury displacement with an apparatus of the type shown in Figure 8. To carry out the measurement, the (evacuated) volume of the empty sample flask is first measured by running a measured volume of mercury from the volumetric bulbs and buret into the flask. The flask volume starts at the midpoint of the capillary tube just below the flask. By adjusting the mercury level in the buret and applying helium pressure or air at atmospheric

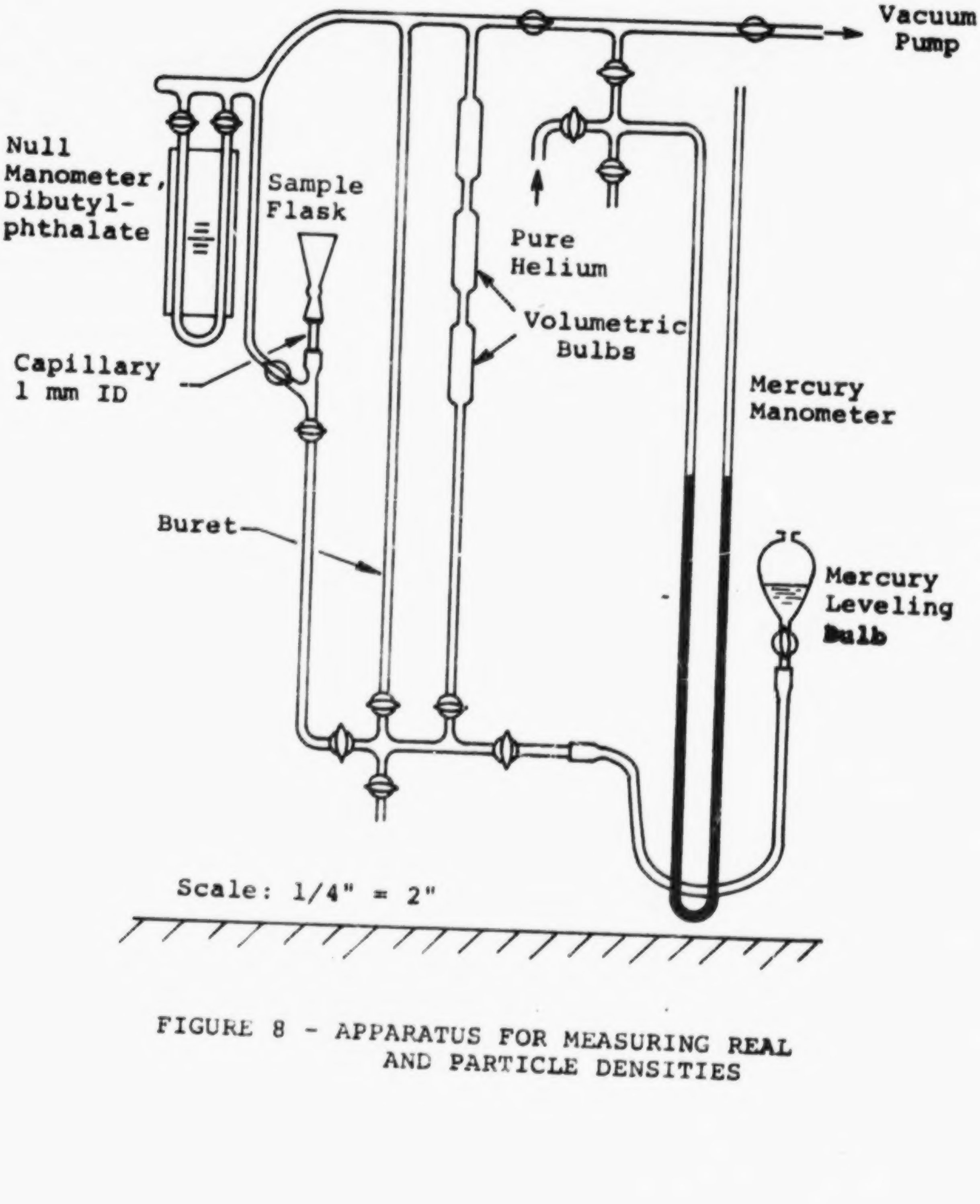


FIGURE 8 - APPARATUS FOR MEASURING REAL AND PARTICLE DENSITIES

pressure to the mercury in the buret, the mercury pressure in the flask is adjusted to 900 mm of mercury. This procedure is repeated with a weighed amount of dry carbon in the sample flask; the mercury volume difference then represents the particle volume of the carbon sample. About 20 to 30 min evacuation time is required to degas the sample sufficiently for an accurate measurement. A final pressure of 900 mm of mercury is required for the mercury to outline the irregular carbon particle surfaces. This pressure is not sufficient to cause mercury penetration into the pores.

The particle density of virgin Filtrasorb 400 is between 0.807 and 0.820 g/cc; ideally, regeneration should attain a density in this range. If a change in particle size distribution occurs in any of the adsorption-regeneration cycles, it may become impossible to attain, simultaneously, a bulk density in the 0.486 to 0.501 g/cc range and a particle density in the 0.807 to 0.820 g/cc range. For the several spent carbons (dried) which have been regenerated during this study, the bulk and particle densities are given below with the calculated bulk volume void space.

For comparison, the void spaces for two virgin Filtrasorb 400 carbons are 0.398 and 0.389 cc/cc bulk volume. The void space of the once-spent Filtrasorb 400 (Table 2) is within the void space range of the virgin carbon, indicating that the particle size distribution of the two are still the same. Spent 17A and V1A carbon have smaller void spaces, indicating that the particle size distributions have shifted. Sieve analyses indicated that the distributions have shifted toward the smaller particle size range. This is a reflection of carbon loss since 17A was regenerated 7 times and spent 8 times and V1A regenerated once and spent twice.

TABLE 2 - BULK AND PARTICLE DENSITIES OF SPENT CARBONS

Carbon	Bulk density g/cc	Particle density g/cc	Void space cc/cc
17A	0.601	0.970	0.381
V1A	0.616	0.990	0.378
Once spent Filtrasorb 400	0.584	0.971	0.398

The void space is calculated with the formula

$$1.000 - \frac{\text{bulk density, g/cc}}{\text{particle density, g/cc}} = \text{void space, cc/cc bulk volume}$$

To determine the particle volume decrease during regeneration, four measurements are required for each run, namely carbon weight before and after the run and particle density before and after the run. For runs 50 and 51, described earlier in Table 1, the necessary quantities and calculations are summarized in Table 3.

TABLE 3 - PARTICLE VOLUME MEASUREMENTS FOR RUNS 50 AND 51

Baking Run 50		
Weight fed to regenerator (V1A), g	1401.0	
Particle density, g/cc	0.990	
Particle volume, cc		1415
Weight of product, g	1230.5	
Particle density, g/cc	0.881	
Particle volume, cc		1397
Particle volume decrease, cc		18
Particle volume decrease, %		1.27
Activating Run 51		
Weight fed to regenerator (raw 50), g	1118.8	
Particle density, g/cc	0.881	
Particle volume, cc		1270
Weight of product, g	993.8	
Particle density, g/cc	0.789	
Particle volume, cc		1259
Particle volume decrease, cc		11
Particle volume decrease, %		0.87
Total particle volume decrease for regeneration		2.14%

A comparison of bulk volume and particle volume decreases, as detailed below, show that the particle volume decrease is larger for both runs.

	bulk volume decrease, %	particle volume decrease, %
Run 50	0.97	1.27
Run 51	0.49	0.87
	1.46	2.14

Over 20 runs each of baking and activating, it was observed that the bulk particle volumes fluctuated with one or the other being larger. The overall averages for the 20 runs each given below indicate that the two methods are comparable for a single regeneration.

	mean bulk volume decrease, %	mean particle volume decrease, %
20 baking runs	1.16	1.15
20 activating runs	0.46	0.97
	1.62	2.12

Eighteen of these regenerations were of VJA and two were of once-spent Filtrasorb 400.

Because the whole sample is measured, bulk volumes can be measured with greater precision than the particle volumes. Because particle volumes are measured on 25 cc sized samples, sampling errors can very easily occur. To avoid sampling errors, the total charge or product is blended and the sample for testing taken with a spoon rather than by pouring.

Real Density Measurements

The real density is measured by helium displacement and includes only the volume of the solid carbon structure. One of the useful applications of real density is that it gives an indication of the state of decomposition of the adsorbate on baking or activation. Real density can also be used, in conjunction with the particle density, for determining the total pore volume.

Real density measurements are made with the same apparatus (Figure 8) that was used for particle volume measurements. The sample flask volume is first measured when empty with helium and again with a weighed carbon sample, the difference in volume being the volume of the solid carbon structure. The sample flask volume includes the tubing to the stopcocks below the flask. The flask, with or without carbon, is first evacuated from 20 to 30 minutes and then both stopcocks below the flask are closed. With mercury levels down, the volumetric bulbs and buret are filled with pure helium at atmospheric pressure. Both stopcocks on the null manometer are opened simultaneously and momentarily to equalize the pressure in the null manometer with the pressure in the rest of the system. The lower left stopcock is opened to let the helium enter the flask. The mercury levels in the volumetric bulbs and buret are raised to increase the helium pressure to the initial pressure as determined by the null manometer. The volume of helium then displaced at constant pressure is the void volume in the sample flask.

The real density of virgin Filtrasorb 400 is 2.15 g/cc, the density a goal of regeneration. This goal, however, is easily attained since, after the baking step, the real density is close to 2.15 g/cc. Real density less than 2.15 g/cc definitely indicates that volatile adsorbates are retained in the carbon. The real densities and pore volumes, as given below, for runs 50 and 51 are typical.

	Real density, g/cc	Pore volume, cc/cc particle vol.
Feed for Run 50 (V1A)	1.88	0.471
Product Run 50	2.14	0.588
Product Run 51	2.16	0.631
Virgin Filtrasorb 400	2.15	0.623

The pore volume is calculated with the formula

$$1.000 - \frac{\text{particle density, g/cc}}{\text{real density, g/cc}} = \text{pore volume, cc/cc particle volume}$$

Iodine Number

Measurement of iodine number is a standard decolorizing test used in the activated carbon industry for liquid phase carbons. It is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration of the residual filtrate is 0.02 normal. The details of this test are given in Appendix A.

At the Pittsburgh Carbon Company[1,2] the iodine numbers of about 34 carbons of several raw materials and several methods of manufacture were correlated with surface area measurements. From this work the following equation was derived which relates the cumulative surface area, of pores larger than 10 Å diameter, with the iodine number

$$Y = 17 + 1.07x$$

where Y is the iodine number and x is the surface area, in square meters per gram carbon, of pores larger than 10 Å in diameter. The coefficient of correlation is 0.97 and standard of error of estimate is 71.5.

The iodine number is used in this program to measure the extent of recovery of adsorptive capacity or, stated in other terms, the extent to which the micropores have been cleared of adsorbate. The micropores are in the 10 to 30 Å diameter range and also contain 95% of the Filtrasorb 400 total surface area. The iodine number of virgin Filtrasorb 400 has been found to vary from 985 to 1020 mg/g for different samples. If 1020 mg/g is used, the surface area of pores larger than 10 Å diameter as calculated with the above equation is 940 m^2/g while the total surface area as measured by nitrogen adsorption, using the BET[3] method, is 1050 m^2/g.

The 985 to 1020 mg/g iodine number range is the fourth goal to be achieved on regeneration. However, it is not implied that the iodine number is a direct measure of the adsorptive capacity for biologically nondegradable molecules present in sewage. Evidence has been presented showing a good correlation between COD adsorption and iodine number.[4] On the other hand, powdered Darco carbons with low iodine numbers have been found to have high adsorptive capacities for these molecules. The iodine test in this program is being used as a gauge to determine the state of recovery of original properties of Filtrasorb 400.

Iodine number measurements for runs 50 and 51, show the progress made during regeneration.

	Iodine number
Feed for Run 50, spent V1A	529
Run 50, product	754
Run 51, product	900

The iodine number of this regenerated product falls short of the virgin carbon iodine number although the bulk and real densities are at the right level.

Molasses Number

The bulk volume decrease and, more reliably, (when the loss occurs by way of particle size decrease), the particle volume decrease measure the carbon loss. Particle size decrease can occur by direct oxidation of the particle outer layers by the activating gases. It can also occur from normal handling attrition if the basic carbon structure has been weakened by internal overactivation. Some of the attrition products, or fines, are discarded by back washing in the contactor, or are carried up the furnace stack.

Internal overactivation manifests itself through increase in macropore volume, i.e., increase of pores larger than 30 Å diameter. During the process of oxidizing the adsorbate residue in the micropores, the activating gases come in contact with the basic carbon structure resulting in enlargement of micropores to macropore size and further enlargement of macropores. This process thins out the pore walls, making the carbon particles more friable or susceptible to attrition.

The molasses number measures the pore enlargement since it has been found that the molasses number relates to the surface area of pores larger than 28 Å diameter (references 1 and 2). The equation showing this relationship is

$$Y = 129 + x$$

where Y is the molasses number and x the surface area in square meters per gram of carbon. Molasses consists of a concentrated sucrose solution with a considerable concentration of color bodies. Although the color bodies are more strongly adsorbed than the sucrose, the large excess of sucrose fills up the micropores thereby greatly slowing up the color body adsorption. An exchange of color bodies for sucrose is slow in the micropores but much faster in the macropores, hence the correlation of macropore area with molasses number.

The molasses number for various virgin Filtrasorb 400 samples has been measured in the range 190 to 216, which is the fifth goal to be achieved during regeneration. Again, using the runs 50 and 51, the progression of molasses number during regeneration is demonstrated.

	Molasses number
Feed for Run 50, spent V1A	172
Run 50, product	198
Run 51, product	262

Although the external burn off of the carbon particles was quite small, the high molasses number of 262 and low iodine number of 900 indicate that internal damage had been done to this carbon on this regeneration or the prior one.

The details of the molasses test procedure are given in Appendix B.

Other Measurements

Two other measurements or computations are necessary to complete the characterization of the regeneration run. These are the carbon residence time in the regenerator and the percentage of external burn off.

The residence time is calculated with the following formula:

$$\frac{V_i - V_e \frac{V_i}{V_p}}{V_f} \times \frac{42}{65} = \text{hours residence time in heated zone of regenerator}$$

where:

V_i = the bulk volume of total charge fed to regenerator

V_e = the bulk volume of product at time feeding was completed

V_p = the total bulk volume of product at completion of run

V_f = the feed rate in consistent unit of volume per hour

42 = the length of the heated zone

65 = total length of the tube

The percent external burn off is calculated with the following formula:

$$\frac{v \times d}{w} \times 100 = \text{percent external burn off}$$

where:

v = the decrease in particle volume during a run

d = the particle density at the beginning of the run

w = the total weight decrease during run

As examples of this calculation, using data from Table 3, the percent of external burn off for runs 50 and 51 are:

Run 50 $$\frac{18 \times 0.990}{1401.0 - 1230.5} \times 100 = 10.4\%$$

Run 51 $$\frac{11 \times 0.881}{1118.8 - 993.8} \times 100 = 7.7\%$$

For run 50, the 10.4% is in reality not a "burn off" since no oxidizing agents were used, but rather indicates that, of the total volatiles evolved, 10.4% came from the exterior of the particles. By difference, 89.6% of the volatiles came from within the pores of the carbon. For run 51, the 7.7% is a measure of loss of basic carbon from the exterior and by difference, 92.3% of the weight decrease comes from oxidation of free carbon adsorbate residue and oxidation of internal carbon structure.

EXPERIMENTAL RESULTS

Parameters Studied

The goals of the regeneration are to remove the adsorbate from the pores of the spent carbon without oxidizing or burning away any of the outer portions of the carbon particles or without altering the basic pore structure. The loss of carbon from the carbon exterior is measured by the change in bulk or particle volume while change in pore structure is indicated by the iodine and molasses numbers. In terms of physical properties of the spent carbon and regenerated carbon, the goals of the program can also be expressed by the desired changes as given in Table 4.

TABLE 4 - DESIRED PHYSICAL PROPERTY CHANGE ON REGENERATION

	Initial spent carbon (V1A)	Regenerated carbon
Bulk density, g/cc	0.616	0.490
Particle density, g/cc	0.990	0.810
Real density, g/cc	1.88	2.15
Pore volume, cc/cc particle volume	0.471	0.618
Iodine number	529	1010
Molasses number	172	200

The properties of the regenerated carbon are those of the virgin Filtrasorb 400.

To accomplish the desired physical property changes, the regeneration studies centered primarily around the areas of activating, baking and drying, with some time devoted to vent gas analysis and effect of quenching on carbon properties. The results are presented below under the following headings:

Low-Temperature Activation with High Gas Input

High-Temperature Activation with High Gas Input

High-Temperature Activation with Low Gas Input

Regeneration of Once Spent Filtrasorb 400

Comparison of Hearth Furnace and Rotary Tube Activation

Baking Temperature Profile

Particle Volume Decrease During Baking

Drying Studies

Effluent Gas Analysis

Quenching Experiments

Low-Temperature Activation with High Gas Input

Since the adsorbate is predominantly in the micropores, the activating gases come into contact with the basic carbon structure before they reach the adsorbate or adsorbate residue. The activating gases first come in contact with the exterior surface of the carbon particles and then the macropore surface before reaching the micropores, where the beneficial oxidative action can take place. Depending on the temperature and other operating conditions, varying amounts of carbon are oxidized from the exterior surface and macropore surface, along with the oxidation of adsorbate or adsorbate carbon residue and micropore surface.

On the basis of thermodynamic calculations, hydrocarbons are oxidized by steam and carbon dioxide at considerably lower temperatures than free carbon such as formed by decomposition of adsorbate or the basic structure of the activated carbon. The extent of this difference is shown in Figure 9. The letter f designates the fraction of influent steam consumed before equilibrium is established while oxidizing n-tetradecyl benzene ($C_{20}H_{34}$), toluene (C_7H_8) or carbon. These molecules represent the adsorbate in regard to oxidative susceptibility. At 800°F and equilibrium conditions, very little of the free carbon is oxidized, while 70% to 95% of the adsorbates are oxidized. The possibility of carrying out the regeneration at this temperature was investigated since it would assure minimum attack on the basic carbon structure. Results are discussed below.

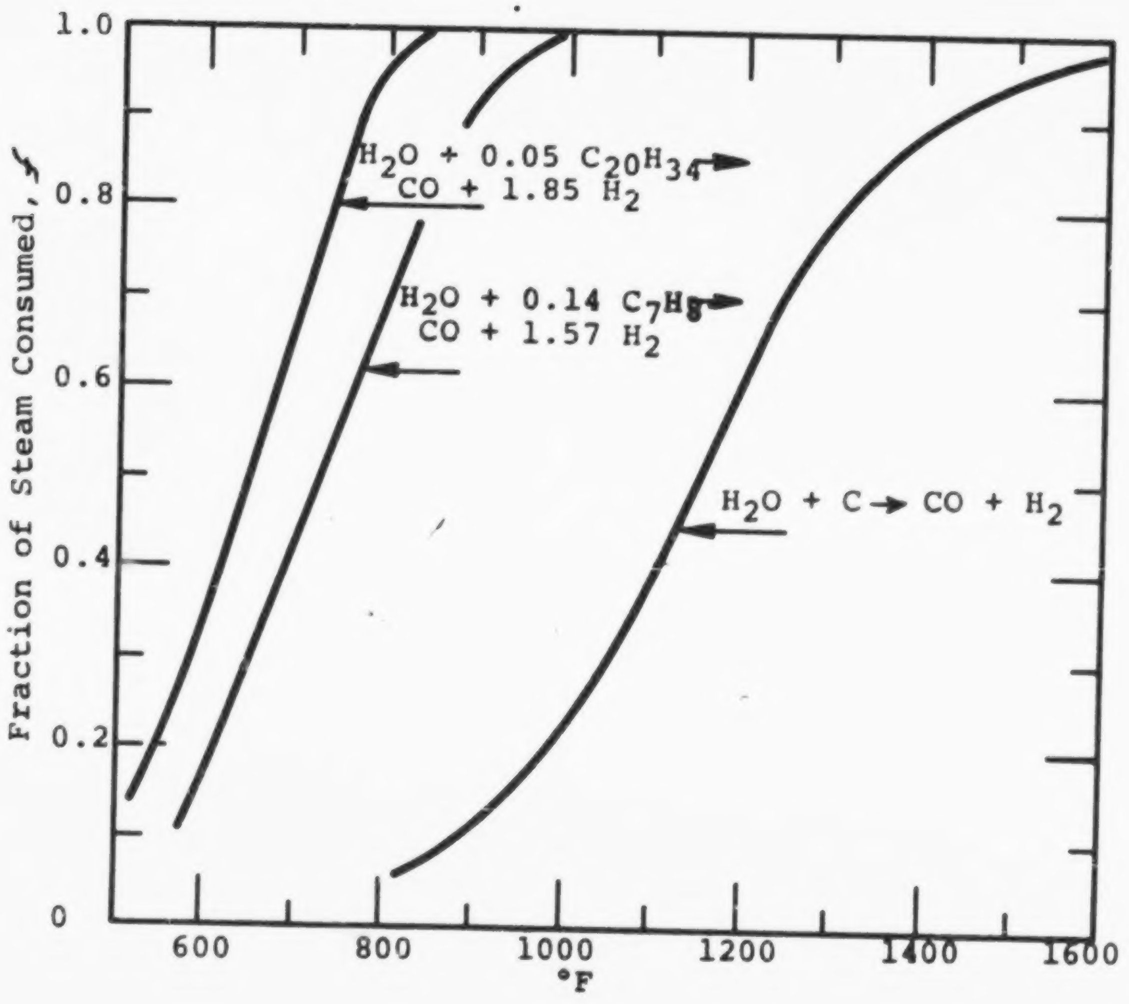


FIGURE 9 - FRACTION f OF STEAM CONSUMED AT VARIOUS TEMPERATURES WHEN REACTION PROCEEDS TO EQUILIBRIUM

In the multiple-hearth furnace, the combined baking and activating time is about 15 minutes and the activating gas temperature about 1700°F. Since the oxidation rates at the 800°F temperature level were expected to be slower, a considerably longer (2 hours) regeneration time was used. The investigation, however, demonstrated that the oxidation rates were quite slow and that the decomposition of the adsorbate to volatiles and free carbon progressed to a larger degree than had been expected.

Table 5 shows the physical property data for two 800°F runs. The feed carbon was 17A that had been dried and prepared according to the previously described charge preparation procedure. For these two runs, and also for the other runs given in Table 5 the gas composition and input rates are given in Table 6. For comparison, the gas composition and input rates are also given for the Pomona multiple hearth furnace during a normal wet spent carbon regeneration. On the basis of per pound of regenerated carbon, the laboratory activating gas input rate was 12.8 ft^3, while for the hearth furnace it was 27.5 ft^3.

TABLE 6 - GAS COMPOSITION AND INPUT RATE

	Laboratory rotary		Pomona hearth furnace	
	std ft^3/hr	std ft^3/lb	std ft^3/hr	std ft^3/lb
N_2	9.3	18.6	2440	27.3
CO_2	1.2	2.4	295	3.3
H_2O	5.2	10.4	2100	23.5
O_2	---	---	67	0.7
Activating gas totals (N_2 not included)		12.8		27.5

Runs 3 and 5 (Table 5), at 800°F, show a decrease in bulk density from 0.608 to about 0.570 g/cc and a particle density decrease from 0.970 to 0.915 g/cc. Considering the long residence time and large activating gas input rate, this is a small loss in the carbon density. Later baking studies definitely indicated that this density decrease was not due to oxidation of the adsorbate but rather to decomposition of the adsorbate. For example, 15-gram samples of dried spent

TABLE 5 - REGENERATION AT LOW TEMPERATURES, 800 to 1500°F

Feed carbon or run no.	Temperature °F	Bulk density g/cc	Particle density g/cc	Real density g/cc	Pore volume cc/cc particle vol.	Bulk vol. decrease %	Weight decrease %
Dried spent 17A, feed for runs 3 and 5	---	0.608	0.970	1.90	0.490	---	---
Run 3 product	800	0.567	---	---	---	---	10.0
Run 5 product	800	0.571	0.915	2.06	0.555	0.6	7.0
Virgin Filtrasorb 400 feed for run 4	---	0.501	0.820	2.15	0.618	---	---
Run 4	800	0.501	0.820	2.15	0.618	0.0	0.4
Dried spent 17A, feed for runs 6, 7 and 13	---	0.605	0.970	1.90	0.490	---	---
Run 6	1000	0.566	0.910	2.07	0.560	0.7	7.7
Run 7	1200	0.553	---	---	---	0.5	8.5
Run 8 (run 7 feed)	1200	0.550	---	---	---	0.6	1.1
Run 11 (run 8 feed)	1400	0.521	---	---	---	0.4	7.4
Run 12 (run 11 feed)	150	0.523	---	---	---	0.05	0.0
Run 13	1500	0.499	0.803	2.10	0.618	1.0	18.6

VlA were heated in an oven for 1.5 hr at 850°F in a nitrogen atmosphere. The samples lost 8.2% in weight, about the same loss as for runs 3 and 5. The particle density decreased from 0.988 to 0.906 g/cc, which are again comparable to runs 3 and 5 decreases.

Run 4, made with the virgin Filtrasorb 400, showed no change except for a small (0.4%) weight decrease, indicating, as could be predicted from Figure 7, that very little oxidation of basic carbon would occur at 800°F.

On runs 6 to 13, the temperature was increased in 100°F and 200°F intervals to determine whether, at which temperature between 800°F and 1500°F, the spent carbon could be regenerated at minimum risk to basic carbon structure. The progression shows that at 1200°F, the regeneration is still essentially a baking action because the bulk density at 1200°F is 0.550 g/cc, comparable to 0.545 g/cc, the latter figure being bulk density of spent carbons baked at a later date at 1600°F. A comparison of runs 7 and 8 show that very little adsorbate can be driven off at 1200°F by increasing residence time an additional two hours. When the temperature is increased to 1400°F, (Run 7) an additional amount of adsorbate is removed in a two-hour period. Part of the removal is due to the baking action and now partly to steam oxidation since the bulk density is down to 0.521 g/cc, i.e., below the 0.545 g/cc baked carbon density at 1600°F.

Run 12 at 150°F was made to determine to what degree the bulk density decreases are due to baking and activating and to what degree to possible mechanical attrition caused by the equipment. The zero weight decrease and the small (0.05%) bulk volume decrease attest to the fact that mechanical attrition loss is nil.

When the temperature was increased to 1500°F (Run 13) the steam oxidation increased considerably, as is indicated by the final bulk and particle densities which are now slightly less than those of the virgin carbon. The iodine and molasses numbers on this run were 520 and 250 respectively. When compared to the 1020 iodine number and 210 molasses number of the virgin carbon, they indicate that a considerable portion of the micropores had become enlarged to macropores. Whether this damage to pore structure was done on this regeneration or on one of the seven previous regenerations, could not be determined. At the Pomona plant, on successive adsorption-regeneration cycles, the iodine number has been observed to decrease from 1097 for the virgin carbon to 655 for the regenerated carbon on the 8th cycle[4], hence the enlargement of pores could have happened earlier.

The low temperature regenerations definitely indicate that at 1400°F and lower, very little or no steam oxidation of the adsorbate occurs even at the extended 2-hour regeneration time and high activating gas input rate. The weight decrease can be accounted for by decomposition and volatilization of the adsorbates. In the temperature interval from 1400°F to 1500°F, the oxidation rate increases rapidly and in a 2 hour regeneration time, considerable amount of adsorbate or free carbon from the adsorbate is oxidized. In the shorter, 11 min, activation time of the multiple hearth furnace, the amount of oxidation occurring at temperatures below 1500°F would, however, still be small compared to the oxidation occurring at temperatures between 1500 to 1650°F.

High Temperature Activation with High Gas Input

Because of rapid carbonizing action occurring at temperatures below 1500°F, the material remaining for the high temperature activation is essentially free carbon, i.e.,carbon residue of the adsorbate and the basic carbon structure. The loss of basic carbon structure cannot then be completely avoided, hence the best that can be expected is to keep the carbon loss at as low a level as possible while removing the adsorbate carbon residue.

Because of the low iodine number (520) on run 13, further studies were carried out with the main purpose being to increase the iodine number. The assumption was made that, at Pomona, on their regeneration of the particular batch received by MSAR, the bulk density had been brought down considerably below the 0.500 g/cc of the virgin carbon. Hence, by regenerating to lower densities the iodine number was expected to increase.

On runs 14 to 17, the temperature was progressively increased while maintaining carbon residence time at 2 hrs and activating gas input as before (see Table 6). The temperatures are recorded in Table 7 and the regenerated carbon properties in Table 8. As the results show, the iodine number did not come up to 1020 although the bulk density was brought down to 0.410 g/cc. The pore volumes were much larger than the 0.619 cc/cc p.v. for the virgin carbon. The high molasses number indicated that the pores of the larger size were developing to the detriment of adsorptive capacity and carbon hardness.

On runs 18 to 24, the carbon residence time was progressively decreased from 2.6 to 0.5 hr while still maintaining activating gas at the prior high input rate and the

TABLE 7 - OPERATING CONDITIONS FOR HIGH TEMPERATURE REGENERATIONS

Feed carbon or run number	Carbon residence, hr	Gas temperature, °F I	Gas temperature, °F II	Gas temperature, °F III	Weight decrease %
Dried spent V1A feed for runs 14 to 18 and 20 to 24	---	---	---	---	---
Run 14	2.0	1500	1500	1500	22.4
Run 15	2.0	1500	1500	1550	25.5
Run 16	2.0	1500	1550	1600	27.0
Run 17	2.0	1550	1650	1600	34.8
Run 18	2.6	1700	1650	1550	37.7
Run 20	1.4	1700	1650	1600	18.3
Run 22	0.9	1700	1700	1600	34.1
Run 23	0.5	1700	1700	1600	30.7
Run 24	0.5	1700	1700	1600	31.6
Virgin Filtrasorb 400 feed for run 19	---	---	---	---	---
Run 19	2.0	1700	1650	1550	18.3

TABLE 8 - PROPERTIES OF SPENT CARBONS REGENERATED AT HIGH TEMPERATURES

Feed carbon or run number	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume, cc/cc p.v.*	Particle volume decrease,%	External burnoff, %	Iodine No.	Molasses No.
Dried spent V1A feed for runs 14 to 18 and 20 to 24	0.617	0.982	1.88	0.477	---	---	529	172
Run 14	0.481	0.755	2.11	0.642	---	---	710	---
Run 15	0.463	---	---	---	---	---	698	306
Run 16	0.456	0.742	2.12	0.649	---	---	690	283
Run 17	0.410	0.634	2.18	0.710	---	---	737	---
Run 18	0.390	---	---	---	---	---	935	388
Run 20	0.415	0.698	2.14	0.674	6.7	17.1	945	326
Run 22	0.418	0.680	2.14	0.683	3.8	9.8	1001	344
Run 23	0.436	0.710	2.15	0.669	4.1	11.6	930	379
Run 24	0.446	0.731	2.13	0.656	4.4	13.3	883	309
Virgin Filtrasorb 400 feed for run 19	0.495	0.820	2.15	0.619	---	---	995	210
Run 19	0.430	0.709	2.15	0.671	4.3	28.6	1160	320

* p.v. = particle volume

temperatures at near the 1700°F level. In these runs the iodine number went through a maximum of 1001 at 0.9 hr residence time and dropped to 883 at 0.5 hr residence time. In this series of runs, the molasses number stayed at a high level, considerably above 300 for most of the runs, again indicating a general shift to pores of larger size and also loss in hardness.

The loss of hardness in these regenerated carbons was quite apparent because they were very dusty in handling. Also on the grinding of samples for iodine and molasses, the samples ground down in less than three hours while the virgin carbon requires 4.5 hr. (Grinding is done in motor driven mortar and pestle.)

To further check the effects of high temperature and high activating gas input on the pore structure of the carbon, a comparison was made between activity of the carbon particle exterior layers and the carbon particle interior. This was done by placing the carbon in a ball mill without balls, but containing shallow flights. The gentle rolling action over a 24-hour period abraded off some of the outer layers of the particles. About 1% of fines was abraded off each sample on each ball mill run. Iodine and molasses numbers were determined for the fines and interior for each carbon. The results of these experiments are given in Table 9. The results show that overactivation proceeds from the outer layers toward the carbon particle center. In the extreme outer layer, the volume of small pores, as indicated by the lower iodine number, is considerably less than in the interior. On the other hand, the activity distribution is more uniform for the virgin Filtrasorb 400. The enlargement of the pores in the outer layers of these regenerated carbons appears to be the cause of the decreased abrasion resistance.

High Temperature Activation with Low Gas Input

During the remainder of the study, starting with run 25, the baking and activating, and also the drying, were carried out as separate runs or operations. In the activating runs, the gas input was drastically reduced, while the gas temperature was maintained at the 1700°F level. All carbon residence times, in the 42 inch heat portion of the tube, were one half hour and less.

Tables 10 and 11 show operating and carbon property data on selected runs on spent V1A that are representative of this study. The baking run is included with the activating run to give the overall results of each regeneration. As is

TABLE 9 - ACTIVITY DISTRIBUTION IN CARBON PARTICLES

Carbon	Iodine number			Molasses number		
	Interior	Fines	Difference	Interior	Fines	Difference
Filtrasorb 400	1020	970	- 50	216	200	-16
Run 20	945	728	-217	326	339	+13
Run 22	1001	706	-295	344	350	+ 6
Run 23	930	727	-203	379	346	-32

TABLE 10 - OPERATING CONDITIONS FOR HIGH TEMPERATURE BAKING AND ACTIVATING

Run No.	Type function	Carbon residence, min	Gas input, std ft^3/hr			Temperature, °F			Weight decrease, %	
			N_2	CO_2	H_2O	TC(1)	TC(2)	TC(3)		
29	baking	30	3.7	---	---	1700	1700	1600	11.5	19.8
30	activating	30	3.7	0.5	1.9	1700	1700	1600	9.4	
31	baking	90	3.7	---	---	850	1320	1600	11.0	21.0
32	activating	23	4.8	0.7	2.5	1700	1700	1600	11.2	
50	baking	30	3.7	---	---	1700	1700	1600	12.2	22.1
51	activating	33	2.8	0.4	2.0	1750	1750	1650	11.2	
58	baking	13	3.7	---	---	1800	1750	1650	14.8	22.7
59	activating	15	4.8	0.7	2.5	1700	1700	1600	9.3	

TABLE 11 - PROPERTIES OF CARBONS BAKED AND ACTIVATED AT HIGH TEMPERATURES

Run No.	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume cc/cc p.v.[1]	Particle volume decrease, %		External burnoff, %	Iodine No.	Molasses No.
29	0.550	0.881	2.14	0.589	0.8	1.9	6.6	832	202
30	0.500	0.807	2.13	0.622	1.0		10.4	864	239
31	0.548	0.877	2.11	0.584	0.6	2.5	1.8	790	176
32	0.490	0.793	2.14	0.529	1.9		19.7	890	216
50	0.547	0.881	2.14	0.589	1.1	1.9	10.4	754	198
51	0.489	0.789	2.16	0.634	0.8		7.7	900	262
58*	0.536	0.878	2.15	0.582	2.3	2.5	14.1	794	220
59	0.485	0.796	2.14	0.628	0.2		1.6	880	259

*Run 58 was rewetted with water and fed wet during baking, hence the lower bulk density than the other baked carbons.

[1] p.v. - particle volume

evident by comparing the gas input rates of Table 10 with those of Table 6, the gas input rates on these runs were reduced by more than one half.

As the residence time or temperature was changed, the gas input rate was changed also so that the final bulk density always came in the range 0.485 to 0.500 g/cc. In the density and pore volume measurements, these regenerated carbons came close to the virgin carbon measurements but the iodine numbers were too low by about 150 units and the molasses numbers too high by about 35 units. The carbon loss, as measured by the particle volume decrease, varied between 1.9 and 2.5%, which are substantial decreases from the 5% and 7% reported for the hearth furnace operations. On run 51, the gas temperature in each section of the rotary tube was increased 50°F. The effect of this increase was to raise the iodine number by about 10 or 20 units to 900 while causing a very large increase in molasses number. On the overall basis the runs that came closest to regenerating the carbon to original virgin state are 31 and 32 as is evident from comparison given below:

	Runs 31-32	Virgin Filtrasorb 400
Bulk density g/cc	0.490	0.486-0.501
Particle density	0.793	0.807-0.830
Real density	2.14	2.15
Pore volume cc/cc particle vol.	0.629	0.623-0.614
Iodine number	890	995-1020
Molasses number	216	190-216

The large divergence here is the iodine number. On all the runs made on this spent carbon V1A, the iodine and molasses numbers could never be matched simultaneously with those of the virgin carbon. It was finally concluded that during the regeneration at Pomona the pore structure on the batch of carbon sent to MSAR had become altered in such a way that the iodine number was low.

Regeneration of Once Spent Filtrasorb 400

Since the iodine and molasses numbers of regenerated V1A could never be brought up simultaneously to those of virgin Filtrasorb 400, we reasoned that some condition in regeneration was out of line or that a complete regeneration was not possible. To resolve the problem, quantities of once-spent Filtrasorb 400, obtained from Pomona, were regenerated under conditions believed to be optimum, as determined from the V1A regeneration. The first quantity of once-spent Filtrasorb 400 was obtained at a time midway through the study and was sufficient in quantity for two regeneration runs. Another larger amount was received toward the end of the program, but time permitted only one run. The operating conditions and regenerated carbon properties for these three regeneration runs are given in Tables 12 and 13. To establish a standard, virgin Filtrasorb 400 was put through the same baking and activating steps.

Physical property comparisons were made on the regenerated products of these three runs and those of the virgin Filtrasorb 400, as given below:

	Means of runs 34 and 36	Run 65	Virgin Filtrasorb 400
Bulk density, g/cc	0.503	0.486	0.486-0.501
Particle density, g/cc	0.830	0.805	0.807-0.830
Real density, g/cc	2.14	2.15	2.15
Pore volume cc/cc particle vol.	0.612	0.625	0.623-0.614
Iodine number	1014	960	995-1020
Molasses number	196	225	190-216

Except for the iodine and molasses numbers for run 65, all the other properties fall within the ranges that had been measured for the virgin Filtrasorb 400. The results definitely indicate that the spent carbon can be regenerated to its original state in one reg eneration as far as it is possible to measure this within limits of experimental accuracy. The regenerations of runs 34 and 36 were accomplished with 2.8% and 2.9% particle volume decrease, respectively, and run 65 with 2.2%.

Another potential carbon loss not measured previously was that due to formation of fines which, in the adsorption part of the cycle, would be flushed out during the back-washing. This loss was expected to be nil on the low gas input activations. A measure of fines formation was made on the regenerated product of run 65 by sieving out the -40 mesh fraction. By weight this was 0.15%. Hence, by including the fines loss, the maximum particle volume decrease amounted to about 3.0%.

The good recovery of the original properties on runs 34 and 36 adds support to the earlier conclusions that basic carbon structure of V1A is not that of the virgin carbon.

Comparison of Hearth Furnace and Rotary Tube Activation

Various comparisons have been worked out on measured, calculated and estimated operating parameters to show the de-

TABLE 12 - OPERATING CONDITIONS FOR BAKING AND ACTIVATING ONCE SPENT FILTRASORB 400

Feed carbon on run no.	Type function	Carbon residence, min	Gas input, std ft^3/hr			Temperature, °F			Weight decrease, %	
			N_2	CO_2	H_2O	TC(1)	TC(2)	TC(3)		
Spent carbon feed for run 33	----	---	---	---	---	---	---	---	---	
run 33	baking	88	2.0	---	---	600	1100	1600	11.7	17.6
run 34	activating	23	3.7	0.5	0.9	1700	1700	1600	6.6	
Spent carbon feed for run 35	----	---	---	---	---	---	---	---	---	
run 35	baking	78	2.0	---	---	600	1100	1600	10.2	15.7
run 36	activating	30	3.7	0.5	0.9	1700	1700	1600	5.5	
Virgin Filtrasorb 400 for run 37	----	---	---	---	---	---	---	---	---	
run 37	baking	76	3.7	---	---	600	1100	1600	1.4	6.1
run 38	activating	30	3.7	0.5	0.9	1700	1700	1600	4.7	
Spent carbon feed for run 64	----	---	---	---	---	---	---	---	---	
run 64	baking	12	4.8	---	---	1700	1700	1600	10.4	17.2
run 65	activating	13	3.6	0.5	1.9	1700	1700	1600	7.5	

TABLE 13 - PROPERTIES OF BAKED AND ACTIVATED ONCE SPENT FILTRASORB 400

Feed carbon on run no.	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume cc/cc p.v.*	Particle volume decrease, %		External burnoff %	Iodine No.	Molasses No.
Spent carbon feed run 33	0.584	0.971	1.88	0.483	----		----	673	174
run 33	0.532	0.871	2.07	0.579	1.3	2.8	12.4	955	193
run 34	0.502	0.825	2.13	0.613	1.5		19.5	1017	192
Spent carbon feed run 35	0.574	0.955	1.89	0.494	----		----	----	----
run 35	0.527	0.866	2.09	0.585	0.9	2.9	8.3	960	190
run 36	0.504	0.835	2.15	0.612	2.0		36.5	1010	200
Virgin Filtrasorb 400, feed 37	0.486	0.807	2.15	0.623	----		----	1020	210
run 37	0.487	0.799	2.15	0.629	0.3	1.1	21.0	1030	207
run 38	0.468	0.767	2.16	0.644	0.8		16.5	1097	244
Spent carbon feed run 64	0.574	0.949	1.94	0.510	----		----	----	----
run 64	0.522	0.863	2.15	0.598	1.4	2.2	13.6	----	----
run 65	0.486	0.805	2.15	0.625	0.8		10.7	960	225

* p.v. - particle volume

gree of difference between the hearth furnace activating conditions and the optimum rotary tube activating conditions.

Carbon Temperature Profiles

Figures 10 and 11 show the measured temperatures of the three furnace sections and gas temperatures in the rotary tube for the activating runs 32 and 34 (23 minutes residence time) and run 59 (15 minutes residence time). The estimated carbon temperature is given by the broken line curve in each figure.

In the first three runs of the program, both carbon and gas temperature were measured, but the measurement of carbon temperatures was discontinued because of frequent breakage of the thermocouples. At the 800°F temperature regeneration, run 3, it was found that at the thermocouple positions TC (1), (2), (3) and (4) (see Fig. 4), the temperature was about 40°F above the carbon temperature and at position TC (5) the gas temperature was 80°F below the carbon temperature. These temperature differences were used as a guide to locate the carbon temperature profiles in Figures 10 and 11.

In Figure 12, the carbon temperature profiles of Figures 10 and 11 are now plotted as function of carbon residence time. For comparison, the calculated carbon temperature profile for the hearth furnace activation obtained from Figure 6, is included. The profiles indicate that on runs 32 and 34 (23 minutes residence time) the carbon is at temperatures 1500°F and above for 16 minutes, while on run 59 (15 minutes residence time) the carbon is at temperatures 1500°F and above for 10.5 minutes. The carbon in the hearth furnace is at temperatures 1500°F and above for 11 minutes. The important difference is that the carbon in the rotary tube is near the 1650°F level for a much longer time than the carbon in the hearth furnace. At the 1650°F, the oxidation rate is considerably faster, hence, in regard to temperature, the rotary tube activation is carried out under more severe conditions.

Another difference is that, in the hearth furnace, the heat is delivered to the carbon solely by the flue gas-steam mixture while in the rotary tube the heat is delivered to the carbon also by direct transfer through the tube wall. The result is that the rotary tube operates with a smaller temperature difference between gas and carbon. The temperature difference is estimated to be around 40 to 50°F in the activating zone, while in the hearth furnace the temperature difference varies from 70 to 200°F.

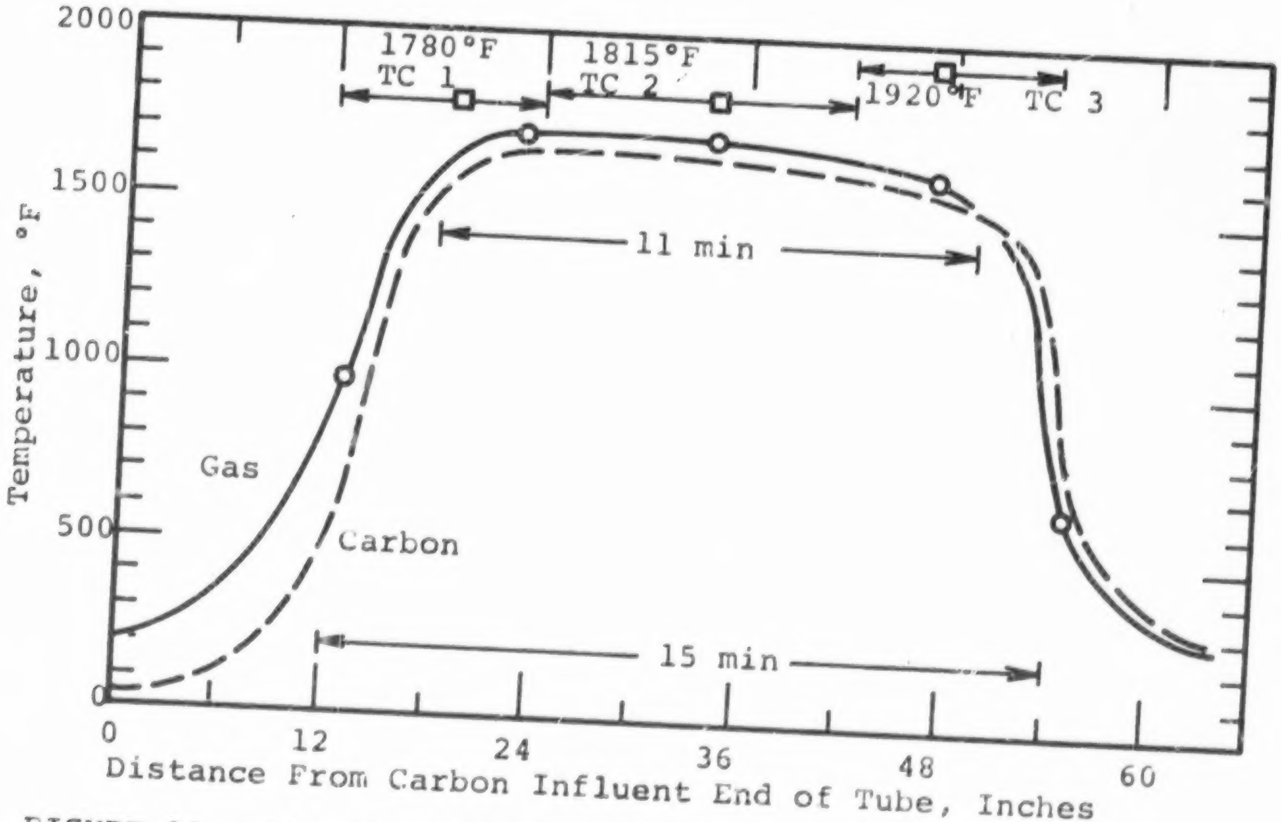


FIGURE 10 - GAS AND CARBON TEMPERATURE PROFILES IN ROTARY TUBE FOR 15 MIN CARBON RESIDENCE TIME, RUN 59

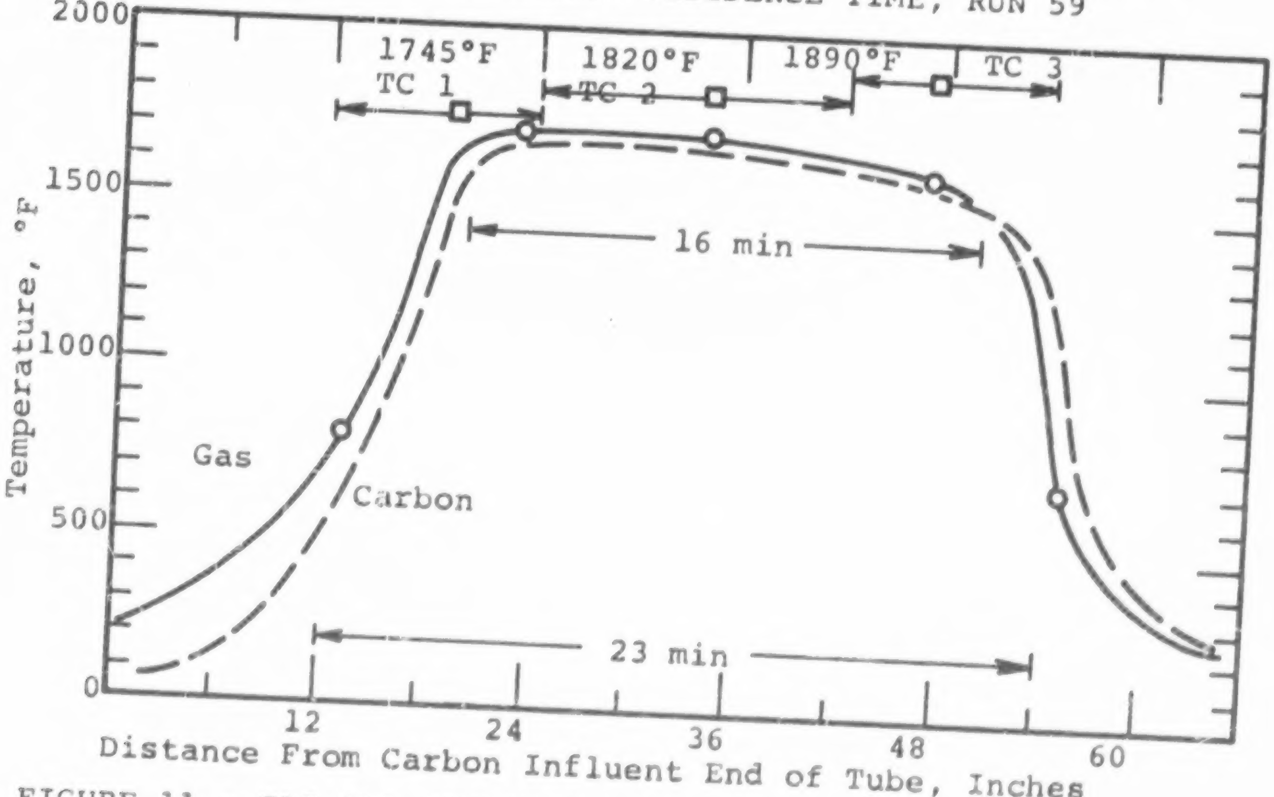


FIGURE 11 - GAS AND CARBON TEMPERATURE PROFILES IN ROTARY TUBE FOR 23 MIN CARBON RESIDENCE TIME, RUNS 32 AND 34

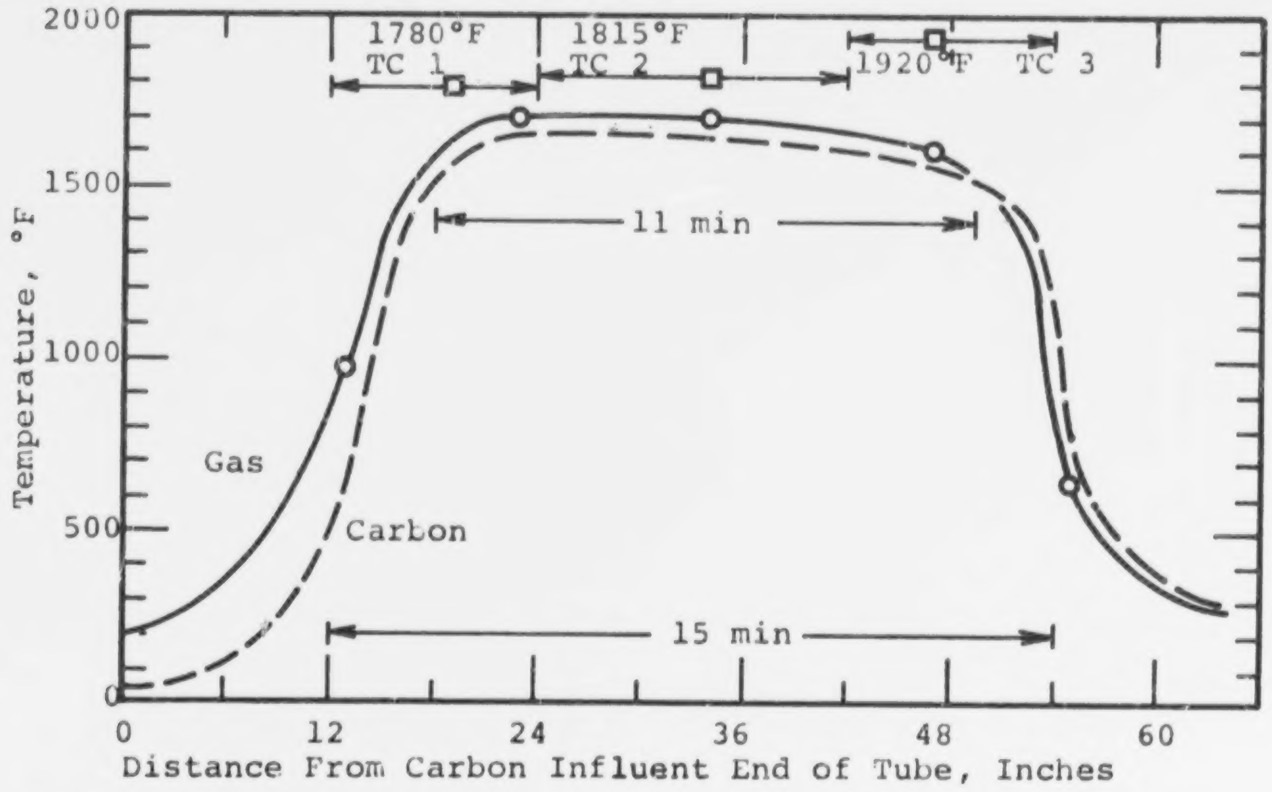


FIGURE 10 - GAS AND CARBON TEMPERATURE PROFILES IN ROTARY TUBE FOR 15 MIN CARBON RESIDENCE TIME, RUN 59

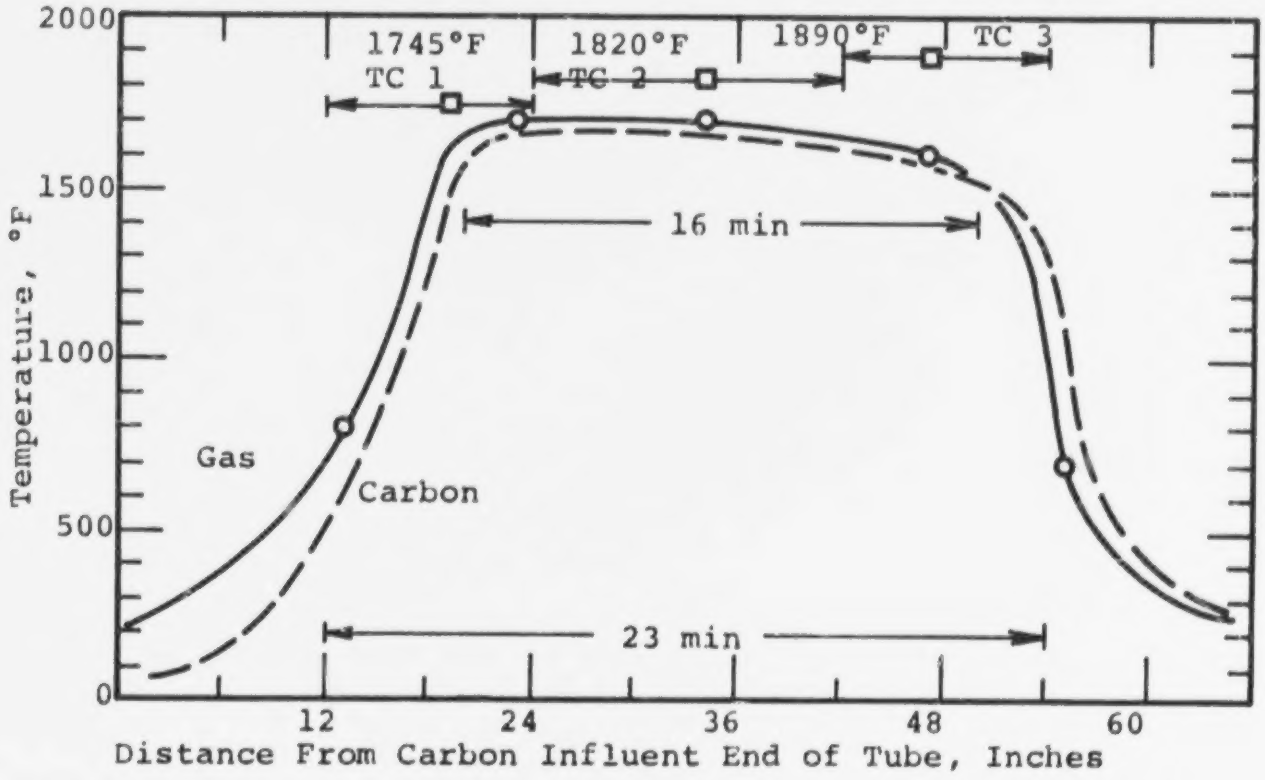


FIGURE 11 - GAS AND CARBON TEMPERATURE PROFILES IN ROTARY TUBE FOR 23 MIN CARBON RESIDENCE TIME, RUNS 32 AND 34

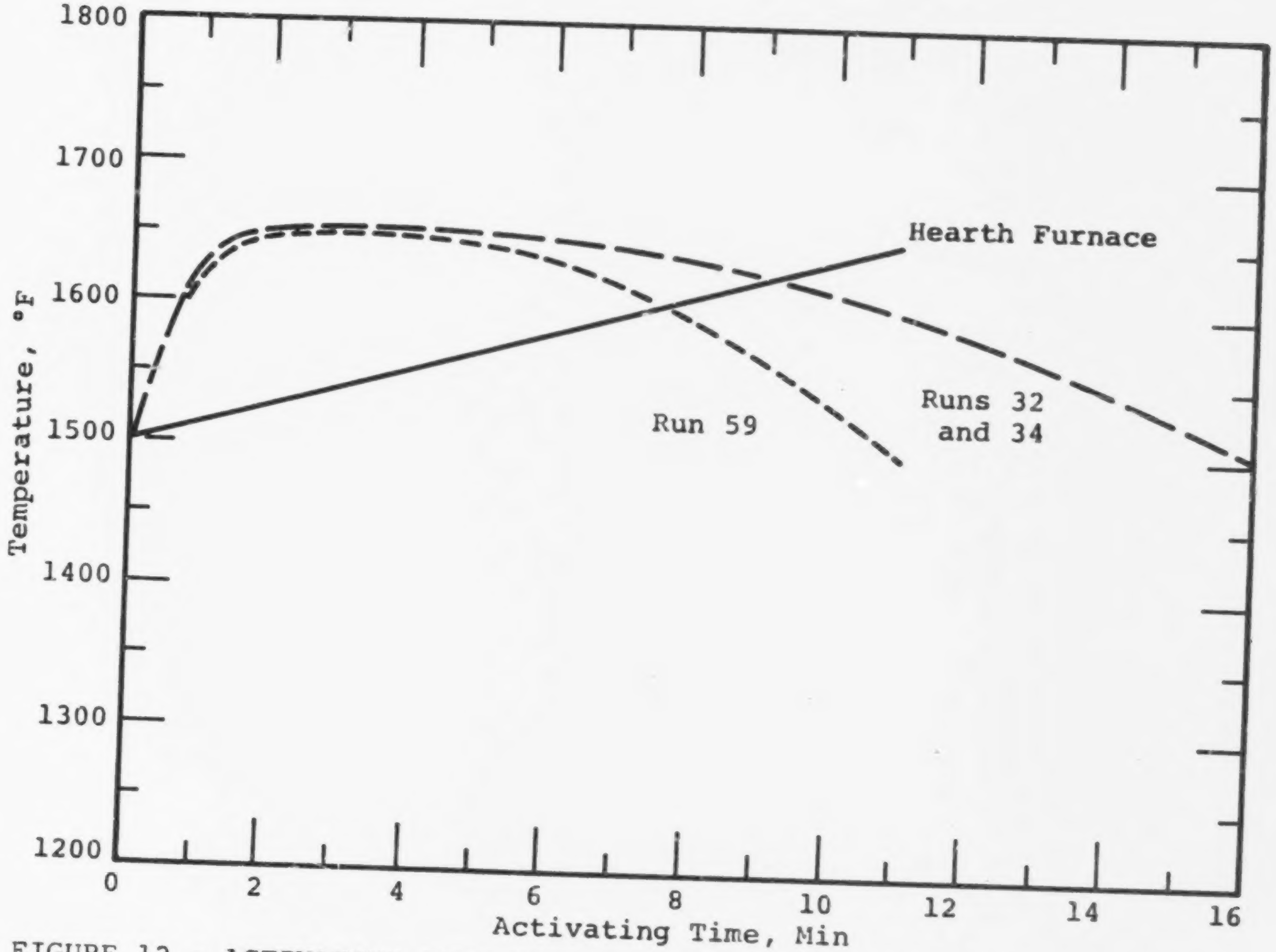


FIGURE 12 - ACTIVATING TIME MULTIPLE HEARTH FURNACE AND ROTARY TUBE
RUN 32, 34 AND 59

Gas Input and Utilization Rates

Table 14 gives the nitrogen and activating gas input rates for five of the rotary tube activating runs and, for comparison, those of the hearth furnace. The activating gas input rate for the hearth furnace is 4.3 to 9.5 times greater than it is for the rotary tube activations. On the other hand, the rate of activating gas utilization for the rotary tube is 2.7 to 4.0 times greater than for the hearth furnace.

TABLE 14 - GAS INPUT AND ACTIVATING GAS UTILIZATION RATES DURING ACTIVATION

	Run 32	Run 59	Run 34	Run 36	Run 65	Hearth furnace
N_2 std ft^3/lb	9.6	9.6	7.4	7.4	7.2	27.3
CO_2 std ft^3/lb	1.4	1.4	1.0	1.0	1.0	3.3
H_2O std ft^3/lb	5.0	5.0	1.9	1.9	3.8	23.5
O_2 std ft^3/lb	0.0	0.0	0.0	0.0	0.0	0.7
Activating gas totals, ft^3/lb	6.4	6.4	2.9	2.9	4.8	27.5
Gas utilization % of input	59	49	78	66	51	18
Carbon weight loss % (based on initial weight)	11.2	9.3	6.6	5.5	7.5	13.4

As brought out in the previous section, the rotary tube activating occurs at a higher temperature but the amount of oxidation is moderated by controlling of activating gas input rate. At the low input rates, the gas utilization rate is high, 47% and greater, which slows down the reaction rate since both the CO_2 and H_2O reactions with carbon are reversible, i.e.,

$$CO_2 + C \rightleftharpoons 2CO$$

$$H_2O + C \rightleftharpoons CO + H_2$$

In the hearth furnace the amount of oxidation in the presence of the large excess of activating gases is controlled by maintaining a lower carbon temperature at which the oxidation rate is slower. Only 18% of the activating gas is utilized. An undesirable characteristic of this method of activation rate control is that the exterior surfaces of the carbon particles are exposed to a high activating gas concentration for the total activating time. By mass action, external burn-off of the carbon particles is accelerated while internal burn-off is relatively slower because of finite diffusion time required for the gases to enter the pores. In the rotary tube, because of the higher temperature, the diffusion rate into the pores is faster thereby accelerating internal burn-off. Because of the low activating gas input rate, the gas composition changes rapidly, thereby decreasing the activating gas concentration in contact with the external surface. External burn-off is thereby minimized.

The carbon weight loss on the once-spent carbons, runs 34, 36 and 65, are in the 5.5 to 7.5% range, compared to 11.2% for run 32 and 13.4% for the hearth furnace activation weight loss. This is due to the smaller initial amount of adsorbate on the once-spent carbons. For the once-spent carbon, the initial density was about 0.587 g/cc and the overall weight decrease on regeneration 17.6%, while for the spent V1A activated in run 32 and also the type activated in the hearth furnace, the initial density was 0.615 g/cc and the total weight loss on regeneration, 21.0%. This points out the necessity of knowing the adsorbate content of the spent carbon feed to permit proper control of the activating gas input rate.

Activating Gas Composition

Table 15 gives compositions of activating gases used in the Pomona hearth furnace and many of the rotary tube runs.

TABLE 15 - ACTIVATING GAS COMPOSITIONS FOR HEARTH ROTARY TUBE REGENERATIONS

	Composition, %				
	Flue gas	Flue gas plus steam	Runs 3 to 24	Runs 32 & 65	Runs 34 & 36
N_2	71.5	49.8	59.2	60.0	71.8
CO_2	8.7	6.0	7.6	8.8	9.7
H_2O	17.7	42.9	33.1	31.2	18.5
O_2	2.1	1.3	0.0	0.0	0.0

Column two gives the flue gas composition of California natural gas burned with 12% excess air of 80% relative humidity. With the 12% excess air, the flue gas contains 2.1% oxygen. Column three gives the mean composition of the flue gas-steam mixture as used in the Pomona hearth furnace. The amount of steam added is based on 0.8 lbs per pound of regenerated carbon.

The activating gases used in the rotary tube are essentially synthetic flue gas mixtures (minus the free oxygen) plus steam added, but not in the amount added at Pomona. For runs 34 and 36, the activating gas is essentially a synthetic flue gas when the natural gas is burned with stoichiometric amounts of air.

Two activations were run in which the activating gas compositions were drastically changed. In run 47, no steam was used and in run 49, no CO_2. The gas compositions used were:

	Run 47	Run 49
N_2	60.8	65.8
CO_2	39.2	0.0
H_2O	0.0	34.2

These runs were made with spent V1A carbon to gain general knowledge on the activation with these two gases and also as an attempt to increase the iodine number of this carbon. The operating conditions of these runs are given in Table 16 and physical properties in Table 17. The corresponding baking runs are included to give the overall results.

Although both activations brought the bulk densities within the virgin carbon range, neither one brought up the iodine number but both brought up the molasses numbers to an excessively high value. On these two runs, the CO_2 activation fared the worst. These results are comparable to the previous runs (Table 11) on V1A, when a synthetic flue gas-steam mixture was used as activating gas. When the water content in the flue gas-steam mixture is at the 30% level, the activating gas, to all practical purposes, acts as a N_2-steam mixture. The steam is a faster acting oxidizing agent and, being in excess, carries the major part of the oxidation load. Vent gas analysis of the N_2-steam activation showed that CO_2 was generated along with the CO and H_2 hence, CO_2 oxidation can be expected to be suppressed when it is present as one of the activating influent gases.

Baking Temperature Profile

During the regeneration series consisting of runs 14 to 24, it became apparent that the adsorbate was carbonized while the carbon temperature was rising from room temperature to about 1500°F, the temperature at which the activating rates become rapid. The carbonization produced a volatile component which was evolved and a free carbon which remained in the pores. In the following activating step the primary objective was to oxidize the carbon residue of the adsorbate with minimum attack on the basic carbon structure.

TABLE 16 - OPERATING CONDITIONS FOR BAKING AND ACTIVATING V1A

Run No.	Type function	Carbon residence, min	Gas input, std ft^3/hr			Temperature, °F			Weight decrease, %
			N_2	CO_2	H_2O	TC(1)	TC(2)	TC(3)	
46	baking	30	4.8	---	---	1700	1700	1600	13.4 } 21.4
47	activating	35	4.8	3.1	---				9.3
48	baking	33	4.8	---	---	1700	1700	1600	13.3 } 23.6
49	activating	44	4.8	---	2.5	1700	1700	1600	11.8

TABLE 17 - PROPERTIES OF BAKED AND ACTIVATED V1A

Run No.	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume, cc/cc p.v.*	Particle volume, decrease, %	Act. gas utilization, %	Iodine No.	Molasses No.
46	0.547	0.873	2.12	0.588	2.1	---	810	219
47	0.498	0.796	2.13	0.626	0.5	49	834	262
48	0.547	0.877	2.14	0.590	2.4	---	802	215
49	0.487	0.776	2.17	0.642	0.3	72	877	288

* p.v. - particle volume

At this stage of the study, it was thought that the manner in which the baking step, i.e., carbonization, was carried out would cause the carbon residue to deposit in different forms. It is apparent that if the carbon residue were in a finely divided form, it would be more easily oxidized while if it formed aggregates or assumed graphitic plates, it would be more difficult to oxidize. The ease or difficulty of the residue oxidation would inversely determine the severity of the required activating conditions and thereby, have an effect on carbon losses.

The study involved heating dried spent V1A at various rates to temperatures above 1500°F and also holding carbon at the maximum temperature for varied lengths of time. The baked materials were then tested and activated under relatively standard conditions to determine ease of activation.

Figures 13 and 14 show temperature profiles for the baking experiments. The profile designated as feed for runs 40 and 41 were baked in an oven in an inert atmosphere. The dried and sieved (14x40 mesh) spent V1A was placed into the oven in shallow trays and heated in each case to 1650°F, according to the time schedule shown in the profile. A nitrogen flow of 5 std ft^3/hr was maintained through the oven during the entire heating and cooling period. The other temperature profiles corresponding to the run numbers were baked in the rotary tube with nitrogen flow, usually 3.7 std ft^3/hr, passed through the tube. Operating and other data are given on some of these runs in Tables 10, 11, 16 and 17.

The results of this study are summarized in Table 18, which gives the heating times to raise the carbon temperature from about 200°F to 1500°F and the lengths of time the carbons were held at 1500°F or above. Although the heating time was varied from 210 to 4 minutes, no trends were indicated in the properties of the baked carbon nor in the iodine and molasses numbers of the corresponding activated products. The maximum deviation from the mean for the densities and pore volumes was of the order of one percent. For the iodine and molasses numbers, the maximum deviation is considerably larger. The means and deviations are as follows:

Baked	
Bulk density, g/cc	0.546 ± 0.004
Particle density, g/cc	0.876 ± 0.007
Real density, g/cc	2.13 ± 0.02
Pore volume, cc/cc particle volume	0.590 ± 0.005
Iodine number	798 ± 44
Molasses number	198 ± 22

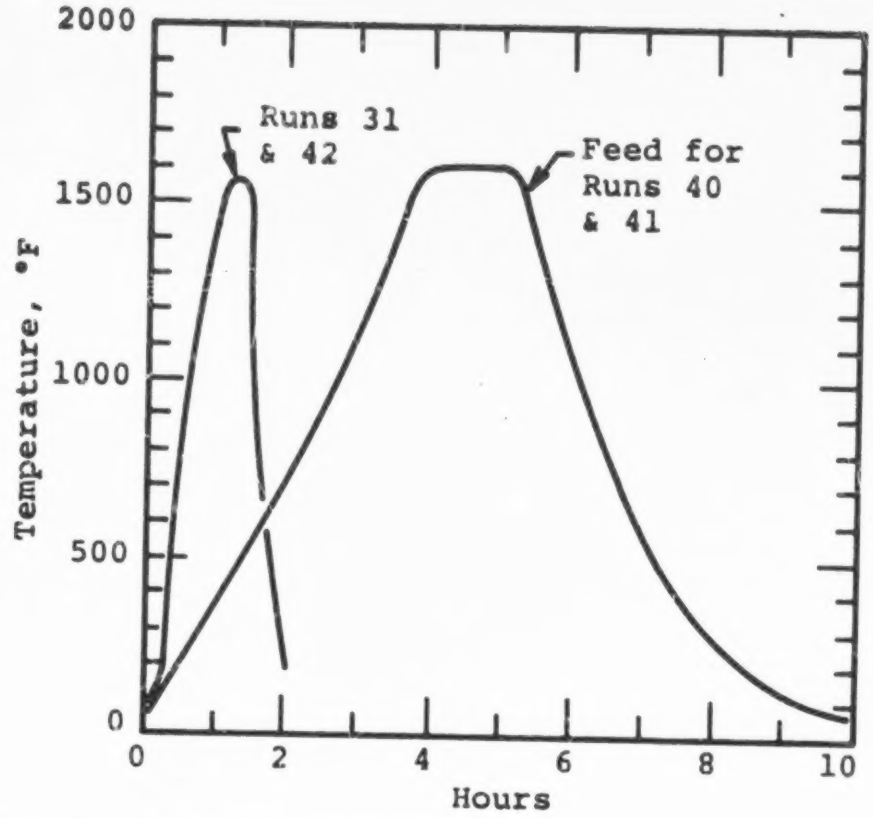


FIGURE 13 - TEMPERATURE PROFILES DURING BAKING OF SPENT V1A

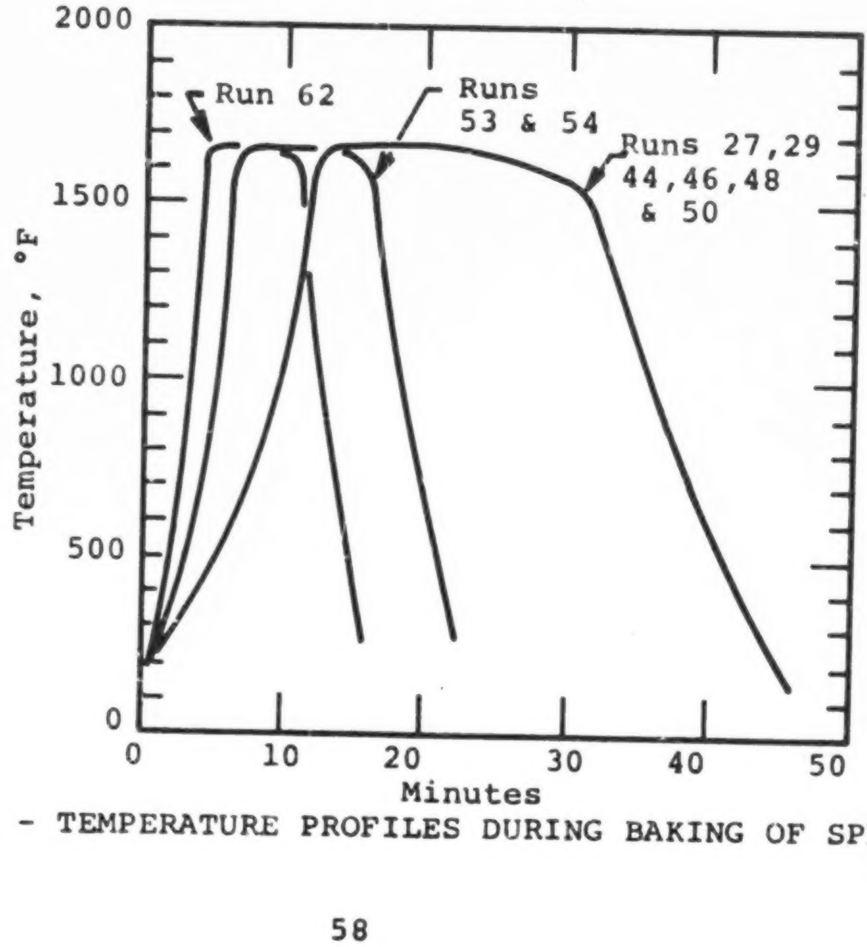


FIGURE 14 - TEMPERATURE PROFILES DURING BAKING OF SPENT V1A

TABLE 18 - PHYSICAL PROPERTIES OF BAKED SPENT V1A

Run No.	Heat time, min	Time at 1500°F, min	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume cc/cc p.v.*	I_2 No.	Molasses No.	After Activation I_2 No.	After Activation Mol. No.
Feed 40	210	90	0.544	0.861	2.15	0.599	780	184	897	235
Feed 41	210	90	0.548	0.877	2.13	0.588	820	202	890	259
31	50	18	0.548	0.877	2.11	0.585	790	176	890	216
42	50	18	0.548	0.876	2.16	0.595	777	176	892	224
27	11	20	0.546	0.873	2.11	0.586	842	205	878	235
29	11	20	0.550	0.881	2.14	0.589	832	202	864	239
44	11	20	0.546	0.878	2.14	0.589	776	171	891	242
46	11	20	0.547	0.873	2.12	0.592	810	219	834 (1)	262 (1)
48	11	20	0.547	0.877	2.14	0.589	802	215	877	288
50	11	20	0.547	0.881	2.14	0.589	754	198	900	262
53	6	10	0.546	0.883	2.14	0.588	774	221	879	290
54	6	10	0.545	0.879	2.12	0.586	820	213	---	---
62	4	7	0.542	0.872	2.13	0.592	794	209	---	---
	means		0.546	0.876	2.13	0.590	798	198	886	249

(1) CO_2 activated, not included in mean values
* p.v. - particle volume

	Activated
Iodine number	886 ± 14
Molasses number	249 ± 33

The mean real density of 2.13 g/cc indicates that the adsorbate residue in the pores is essentially free of carbon since the real density of the virgin carbon is 2.15 g/cc. The mean pore volume of 0.590 cc/cc particle volume is 0.028 cc/cc particle volume smaller than the mean 0.618 cc/cc particle volume for the virgin carbon (see Table 4). The 0.028 cc/cc particle volume is an approximate measure of the carbon residue volume. The mean molasses number (198) for the baked carbon is already very close to the mean virgin carbon molasses number and is a good indication of enlarged pores in spent V1A.

The 6 and 4 minute heating-up times for runs 53 and 62, respectively, are comparable to the 4 minute baking period calculated for the hearth furnace (see section on multiple hearth furnace regeneration). One conclusion that can be drawn from these experiments is that the manner in which the carbon is baked, whether in the rotary tube or hearth furnace, has no significant effect on the baked or activated product.

Particle Volume Decrease During Baking

During baking, a particle volume decrease occurs although the neutral atmosphere precludes possible oxidation of carbon particle outer layers. Other causes for the particle volume decrease have been investigated, i.e., (1) possible shrinkage of the carbon particle due to adsorbate removal and (2) removal of sewage residue adhering to the exterior surface of the particles. In either case, the particle volume decrease as measured is not a true measure of carbon loss.

The list of representative runs given in Table 19 shows a mean particle volume decrease of 1.3% for the spent V1A while the particle volume decrease for virgin Filtrasorb 400 is 0.3%. By difference, the particle volume decrease due to the presence of adsorbate is 1.0%. This amount, subtracted from the previously reported overall particle volume decreases of 1.8% to 3.0%,would give the true carbon losses as 0.8% to 2.0%.

Efforts to determine whether the decrease is shrinkage or residue removal were conclusive but did demonstrate the fact that the volume decrease is not due to mechanical attrition in the rotary tube or formation of fines by rapid expulsion of adsorbate from the carbon. The fines thus formed could be carried out of the regenerator by the sweep gas.

TABLE 19 - PARTICLE VOLUME DECREASE DURING BAKING IN ROTARY TUBE

Run No.	Particle volume decrease, %	Run No.	Particle volume decrease, %
25	1.4	52	1.1
27	1.9	53	1.2
29	0.8	54	0.8
31	0.6	mean	1.3
42	0.7		
44	1.6	virgin Filtrasorb 400	0.3
46	2.1		
48	2.4		
50	1.1		

Two experiments related to particle volume decrease have already been reported in part in the sections "Regeneration at Low-Temperature and High-Gas Input" and "Baking Study". The first experiment involved the two 15g samples of spent V1A carbons which were heated in a stationary oven to 850°F for 1 1/2 hrs in an atmosphere of nitrogen. No particle volume decrease was observed. The weight decrease was 8.2% and the real density was 2.01 g/cc. The low real density indicates that the adsorbate was not completely carbonized, hence, the lack of particle volume decrease may be due to sufficient adsorbate remaining in the pores to prevent volume decrease. In this case, any sewage residue adhering to the outside surface of the carbon particles would be more free to volatilize than the constricted adsorbate in the pores. Since no particle volume decrease was observed, the implication is that the particle volume decrease is not due to loss of exterior residue.

The other experiment involved the feed for runs 40 and 41. In this case, larger quantities of spent V1A were baked in the oven to a maximum temperature of 1650°F in an atmosphere of nitrogen. The results of these baking experiments were:

	Real density, g/cc	Particle volume decrease, %	Weight decrease, %
feed to run 40	2.15	0.5	11.5
feed to run 41	2.13	1.1	11.6

The 11.5 and 11.6% weight decreases in these two runs indicate that considerably more adsorbate was carbonized than during the prior 850°F baking experiment. The real densities of 2.15 and 2.13 g/cc also indicate that the residue from the adsorbate is essentially free carbon. The 0.5 and 1.1% particle volume decreases are comparable to those of Table 19, all of which were baked in the rotary tube. The experiment indicates that the particle volume decrease is associated with temperature above 850°F, but does not differentiate between shrinkage and residue removal.

In these experiments there was no possibility of loss by mechanical attrition since the carbon was held stationary in trays. The slow heat-up rate (210 minutes) is not conducive to rapid expulsion of adsorbate volatiles, thereby creating fines and aiding in their expulsion from the trays. Loss of fines by carry-over with the nitrogen sweep gas would be nil because of the low (5 ft^3/hr) flow rate relative to the large oven volume (4.3 ft^3). The decrease of particle volume due to these causes had been considered a distinct possibility with the rotary tube. Since the particle volume decreases by the two methods are comparable, the carbon losses due to these causes for the rotary tube are now considered quite small.

Drying Studies

In the multiple hearth furnace, the wet carbon is dried on the first three hearths in 15 minutes by contact with gases at 600 to 1300°F. The final temperature of the carbon at the end of the drying period is about 212°F.

Most of the drying for the laboratory rotary tube runs was done in a small laboratory hot air convection oven set at 150°C. About 3 liters of carbon, as received from Pomona, were equally divided between four 1-liter beakers and kept in the oven for about 48 hours. After 24 hours, the carbon in each beaker was turned over so that the carbon that was at the bottom during the first 24 hours was at the top for the second 24 hours. The spent carbon as received from Pomona was sometimes wet and sometimes partially dried. No check was made as to the efficiency of this drying procedure, but it appeared satisfactory because the bulk densities of the dried carbons were very consistent.

Two runs were made wherein the drying and baking were combined to greatly accelerate the drying. In each case, the spent carbon was first dried in the preceding manner and the necessary bulk volume and weight measurements made. A quantity of water was added to each charge which would fill the pores yet leave the carbon in a free flowing state. The water content was 31% on the wet-weight basis. For comparison, the wet carbon fed to the Pomona furnace is about 40% water on the wet-weight basis.

The operating conditions and the carbon properties of these two runs and also the corresponding activating runs are given in Tables 20 and 21. The combined drying and baking time for run 55 was 17 minutes and for run 58, 13 minutes. This is shorter than the combined time for the hearth furnace which is 19 minutes, hence, the drying times in the rotary tube can be assumed to be considerably shorter than 15 minutes. In run 55, the gas temperatures in the three sections I, II and III were 1700, 1700 and 1600°F respectively. At these baking temperatures, the bulk density of the baked product was 0.538 g/cc and the particle density was 0.863 g/cc. For the oven dried spent carbons baked at the same temperature, these densities were normally 0.546 and 0.876 g/cc (from Table 18). Rapid drying then caused a greater evolution of absorbate volatiles. On run 58, an attempt was made to further increase the volatilization of adsorbate by raising the gas temperatures in the three sections to 1800, 1750 and 1650°F and shortening the residence time to 13 minutes. Section I of the rotary tube, where the gas temperature is 1800°F, is the carbon influent end, hence the wet carbon in 5 minutes comes in contact with gas at 1800°F and a tube wall that may be over 1800°F. The increase in severity of baking, however, produced no increased adsorbate volatilization. In regard to iodine and molasses numbers for both the baked and activated products, there was no improvement. These are essentially at the levels shown in Table 18 for the oven-dried spent V1A.

During wetting and drying of the spent carbon feed, the carbon lost weight on each wetting and drying cycle. This treatment was repeated in the hopes that it would lead to a non-destructive way of regenerating spent V1A. It is important to know the nature of the basic carbon structure of V1A since a great deal of work had been done with it.

In this study, an initial 2,450 cc bulk volume of oven-dried carbon was alternately wetted with 670 cc water and dried for 12 cycles. On the 12th cycle, the density appeared to level off at 0.570 g/cc, far from the 0.490 final density so the study was discontinued at this point. The results of the series of experiments are plotted in Figure 15. On each cycle, the wet period or equilibration time was two days and the drying time one to two days in the laboratory oven set at 150°C.

TABLE 20 - OPERATING CONDITIONS FOR RAPID DRYING OF WET SPENT V1A

Run No.	Type function	Carbon residence, min	Gas input, std ft^3/hr			Temperature			Weight decrease, %	
			N_2	CO_2	H_2O	I	II	III		
55	dry & bake	17	3.7	---	---	1700	1700	1600	11.27	21.5
57	activating	30	4.2	0.6	1.4	1700	1700	1600	9.3	
58	dry & bake	13	8.0	---	---	1800	1750	1650	14.8	22.7
59	activating	15	4.8	0.7	2.5	1700	1700	1600	9.3	

TABLE 21 - PROPERTIES OF BAKED AND ACTIVATED V1A AFTER FAST DRYING

Run No.	Bulk density, g/cc	Particle density, g/cc	Real density, g/cc	Pore volume, cc/cc p.v.*	Particle volume decrease,%		Iodine No.	Molasses No.
55	0.538	0.863	2.13	0.594	0.6		813	214
57	0.488	0.776	2.15	0.638	---		904	257
58	0.536	0.878	2.15	0.591	2.3	2.5	794	220
59	0.485	0.796	2.14	0.628	0.2		880	259

* p.v. - particle volume

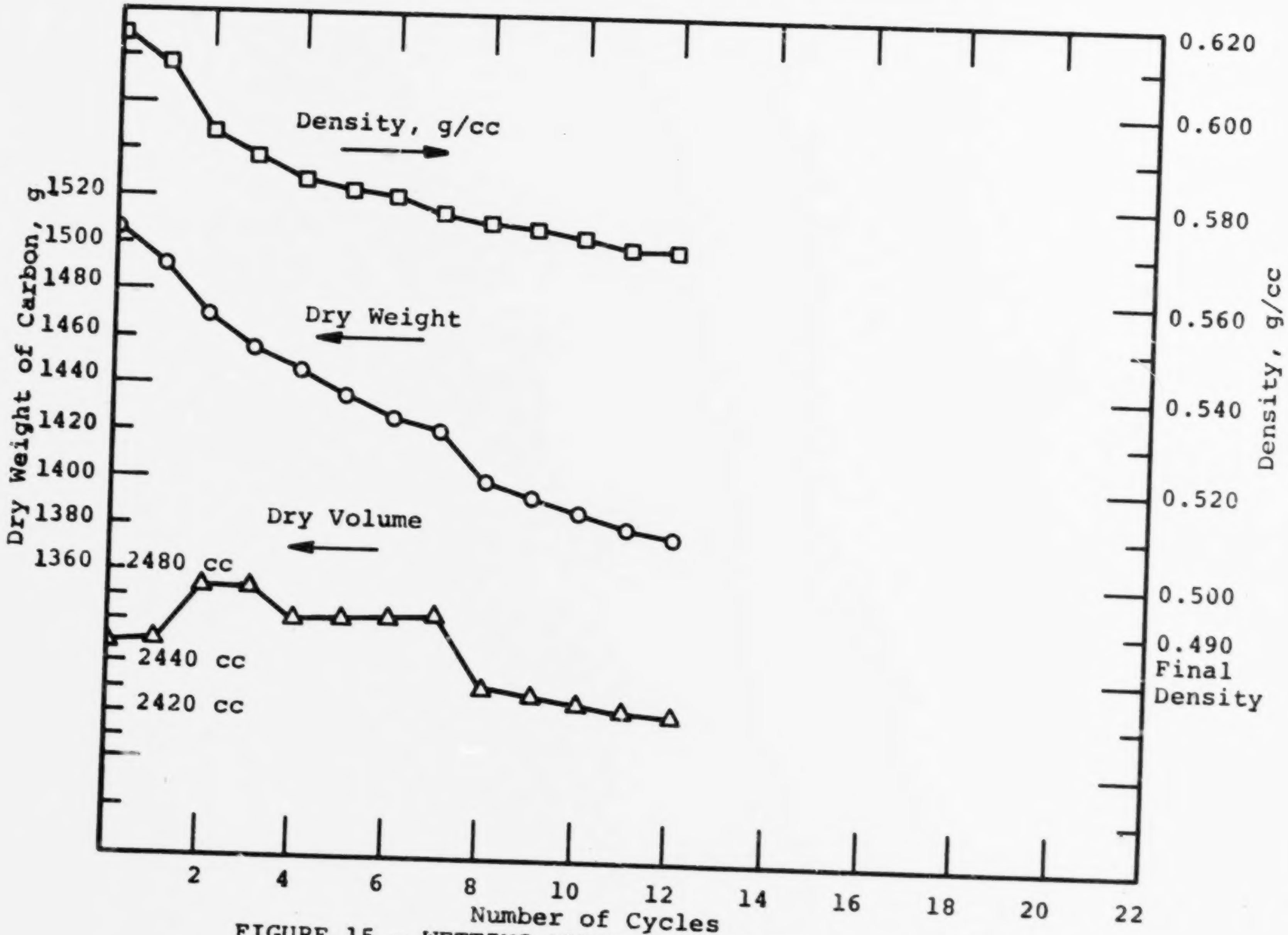


FIGURE 15 - WETTING-DRYING EXPERIMENT ON SPENT V1A

On the second cycle, the carbon became covered with a white powder and the bulk volume increased to 2.740 cc, i.e., by 11.8%. The powder, leached from the interior of the particles, adhered to their exterior and caused an apparent particle volume increase. The powder persisted to varying degrees up to the seventh cycle. On the eighth and subsequent cycles the carbon was leached on a Buchner funnel with 3.5 liters of water before drying. The leaching on the eighth cycle brought the bulk volume down to 2,433 cc, which was below the initial volume by 0.7%. On each of the subsequent cycles, the bulk volume decreased by a diminishing amount until, on the 12th cycle, the volume decrease was 2 cc or 0.04%. The final bulk volume decrease from the original was 28 cc or 1.1%.

Although this experimental study did not lead to a non-destructive means for regeneration of V1A, it produced the first directly measured evidence of change in carbon volume caused by sewage residue adhering to the exterior surface of the carbon particles.

Effluent Gas Analyses

Analysis of vent gas offers a means for monitoring the activating step of the overall regeneration process. In the hearth furnace, the gas sample for activation control should be withdrawn from the fourth hearth at a point where none of the adsorbate volatiles are present but where the activation is essentially completed.

Vent gases have been analyzed on most of the rotary tube activation runs. Some results have been encouraging although problems still exist. As examples of the type of results obtained, calculations are presented on three typical activation runs - runs 45, 47 and 49.

On run 45, the effluent gases are not in correct proportions to represent any possible equilibrium condition with the carbon. This becomes apparent from the following calculations.

TABLE 22 - VENT GAS ANALYSIS OF ACTIVATION RUN 45

Gas	Input, gram moles/hr	Output (dry), gram moles/hr
N_2	6.07	6.07
CO_2	0.88	0.61
H_2	----	2.01
H_2O	3.16	----
CO	----	2.00

On this run, the carbon weight decrease is 30 g/hr or 2.5 gram moles/hr. This weight decrease had to go by way of the following two oxidation reactions:

$$H_2O + C = CO + H_2 \qquad \text{(Eq. 1)}$$

$$CO_2 + C = 2CO \qquad \text{(Eq. 2)}$$

By inspection of the data it is apparent that there is insufficient CO in the vent gas. If only reaction (1) occurred, the amount of CO in the vent gas should be 2.5 gram moles/hr. If only reaction (2) occurred, the amount of CO should be 5.0 gram moles/hr. Since both reactions are known to occur, the amount of CO should be between 2.5 and 5.0 gram moles/hr instead of the 2.00 gram moles/hr as measured.

On run 47, where only CO_2 and N_2 were fed to the regenerator, the input gas composition and dry output gas analysis are as follows:

TABLE 23 - VENT GAS ANALYSES OF ACTIVATION RUN 47

Gas	Input, gram moles/hr	Output (dry), gram moles/hr
N_2	5.95	5.95
CO_2	3.92	1.45
CO	----	3.89

On this run, the carbon weight decrease is 23 grams/hr or 1.92 gram moles/hr. In this case, the gram moles of carbon oxidized per hour agrees with the amount of CO formed, i.e., 2 x 1.92 = 3.84 grams moles/hr of CO. However, the amount of CO_2 consumed indicates that 4.94 gram moles/hr of CO should have been formed instead of the 3.89 gram moles/hr as measured.

On run 49, where only H_2O and N_2 were fed to the regenerator, the input gas composition and dry output gas analysis are as shown in Table 24. The weight decrease on this run is 25.6 grams/hr or 2.13 gram moles/hr. In this case, the water reacts with carbon to form CO and CO_2 according to equation (1) and to equation (3), below:

$$2H_2O + C = CO_2 + 2H_2 \qquad \text{(Eq. 3)}$$

According to equation (1), the gram moles of carbon oxidized and CO generated are the same, i.e., 1.68 gram moles. By equation (3) another 0.42 gram moles is oxidized, giving a total of 2.10 gram moles/hr which is in good agreement with the observed 2.13 gram moles/hr carbon burnoff. In this case, the amount of H_2 generated is short of the amount that should have been generated according to the amounts of CO and CO_2 generated. The amount of hydrogen should have been 2.52 gram moles/hr instead of the 1.89 gram moles/hr as measured.

TABLE 24 - VENT GAS ANALYSES OF ACTIVATION RUN 49

Gas	Input, gram moles/hr	Output (dry), gram moles/hr
N_2	5.95	5.95
H_2O	3.02	----
CO_2	----	0.42
CO	----	1.68
H_2	----	1.89

Probable causes of some of the discrepancies observed above are (1) reaction of the vent gases with the copper vent lines and (2) inaccuracies in CO_2 and N_2 influent measurements.

Quenching Experiments

At the Pomona plant, it has been observed that the iodine number of quenched regenerated carbons is lower than that of regenerated carbons which have been cooled more gradually in an inert gas atmosphere. According to Figure 2 of the May, 1967 Pomona Monthly Report, this difference varies from 50 to 100 iodine number units.

Quenching experiments were performed with virgin Filtrasorb 400 to check out the loss in iodine number and relate it to possible changes in pore structure. Seven experiments were conducted, the first four with a 16x20 mesh sieve fraction and the last three with a 14x40 mesh sieve fraction. In each experiment, the carbon was heated to about 1750°F in a retort in a nitrogen atmosphere and then let fall into water at room temperature. In one experiment the hot carbon was dropped into a container flushed with nitrogen to get a comparison of the effects produced by slow cooling.

The results of the experiments are given in Table 25. They show a general decrease of 25 to 69 iodine units for the water quenched samples. An exception is experiment II, where no decrease was observed. Nitrogen quenching (experiment IV) caused a 23 unit increase in iodine number. The molasses numbers show a maximum deviation of ± 15 about the mean 200 value but indicate no trend or correlation with the iodine number. The first four samples show some pore volume fluctuations which, however, do not correlate with the iodine numbers or molasses numbers. In the last three samples, the pore volume shows little or no change due to the quenching. At present, there is no explanation for the foregoing results. They are offered here solely as recorded observations.

TABLE 25 - RESULTS OF QUENCHING EXPERIMENTS WITH FILTRASORB 400

Exp. No.		Sieve fraction	Weight, g	Pore volume cc/g	Iodine No.	Molasses No.
I	b(1)	16x20	30.0	0.742	1000	185
	a		30.0	0.716	960	220
	c		0.0	-0.026	- 40	+ 35
II	b	16x20	30.0	0.742	1000	185
	a		30.0	0.757	1000	210
	c		0.0	+0.015	0	+ 25
III	b	16x20	30.0	0.759	1002	205
	a		30.0	0.772	944	186
	c		0.0	+0.013	- 58	- 19
IV	b(2)	16x20	30.0	0.760	1002	205
	a		30.0	0.749	1025	210
	c		0.0	-0.011	+ 23	+ 5
V	b	14x40	30.00	0.747	985	214
	a		29.84	0.747	960	191
	c		- 0.16	0.000	- 25	- 23
VI	b	14x40	30.00	0.740	990	194
	a		29.90	0.741	955	205
	c		- 0.10	+0.001	- 35	+ 11
VII	b	14x40	30.00	0.742	984	192
	a		29.50	0.749	915	---
	c		- 0.50	+0.007	- 69	---

(1) Letter b indicates initial sample before quenching, (a) after quenching, and (c) change in properties.

(2) Sample IV cooled in nitrogen.

HEARTH FURNACE THERMODYNAMICS

Material and Heat Balance

On the basis of the operating data obtained from Pomona on the regeneration of wet spent carbon and the information obtained from the laboratory rotary tube runs, the material and heat balance and the carbon temperature profile have been calculated for the regeneration of:

1. Wet spent carbon
2. Dried spent carbon
3. Baked spent carbon

The thermodynamic calculations were made for 2 and 3 above to determine the effect decreased heating loads would have on the required heating gas and steam input rates. In the wet spent carbon regeneration, the gas-steam input rate is excessive in terms of the activation step such that the activation rate must be kept under control by keeping carbon temperature low.

The following are the measured operating conditions and assumptions used in the calculations:

1.	Carbon discharge rate	89.4 lb/hr
2.	Natural gas input rate	270 ft^3/hr @ 60°F
3.	Air input rate:blower cap.	10,800 ft^3/hr @ 60°F
4.	Steam input rate 0.81 lbs/ lb carbon	71.5 lb/hr
5.	Steam generator operating pressure,	10 psi
	estimated steam temperature at hearths	220°F

6. Natural gas composition:

Component	mole fraction
CH_4	0.8721
C_2H_6	0.0806
C_3H_{10}	0.0178
C_4H_{10}	0.0016
CO_2	0.0048
O_2	0.0000
N_2	0.0229
He	0.0002
Sulfur	0.18 grains per 100 SCF

7. Measured gas temperatures on hearths

Hearth	°F
1	600
2	800
3	1000
4	1680
5	1710
6	1720

8. Shell temperature 300 to 400°F.
9. Carbon effluent temperature, (assumed) 1650°F
10. Effluent gas temperature 600°F
11. Carbon influent temperature 70°F
12. Oxygen in flue gas, 12% excess air 2%
13. Burners 4, 5 & 6th hearths
14. Steam distribution to hearths 20% to 4, 40% to 5 and 40% to 6
15. Flue gas distribution to hearths 1/3 to each
16. Weight water evaporated during drying 77.5 lb/hr
17. Weight decrease during baking 13.2 lb/hr
18. Weight decrease on oxidation of adsorbate residue
19. Carbon loss due to activation 7.6 lb/hr
20. Composition of adsorbate volatiles (from rotary tube vent gas analysis) 6.3 lb/hr

Component	Composition,%
CO	35.6
CO_2	16.4
H_2	48.0

21. Estimated heat of adsorbate decomposition at 1400°F - +900 Btu/lb

By means of well known principles of thermodynamics and the above data, the material and heat balance was calculated for the regeneration of wet spent carbon as given in Table 26. The heat loss is obtained by difference and appears to be small for this size furnace. An 8% heat loss would not be out of line. This may be an indication that the estimate for the heat of adsorbate decomposition is too high. The heat balance shows that 77.9% of the heat input comes from the natural gas combustion and 21.7% from the steam input. About 27.0% of the heat input is used for drying, 5.5% for decomposition and volatilization of adsorbate and 63.1% for activation and heating of carbon.

TABLE 26 - MATERIAL AND HEAT BALANCE FOR REGENERATION OF WET SPENT CARBON

		Input			
Material	lb/hr	lb moles /hr	Temp., °F	Btu /hr	Heat, %
Spent carbon, dry	116.5		70	300	0.1
Water in carbon	77.5		70	800	0.2
Activating steam	71.5	3.97	220	5,200	21.7
ΔH_v				75,800	
Natural gas	12.9	0.714	60	000	
ΔH_c				290,800	77.9
Air	237.8	8.26	60	000	
	516.2			372,900	99.9
		Output			
Regenerated carbon	89.4		1650	65,300	17.5
Water from carbon	77.5	4.30	600	18,500	27.0
ΔH_v				82,100	
Volatile adsorbate					
ΔH_d				18,700	5.5
CO	7.4	0.26	600	1,000	
CO_2	5.1	0.12	600	700	
H_2	0.7	0.35	600	300	
Gas from activation					
ΔH_a				26,600	45.6
N_2	180.5	6.45	600	23,900	
CO_2	42.5	0.96	600	5,300	
H_2O	82.4	4.58	600	19,700	
ΔH_v				87,400	
CO	27.4	0.98	600	3,700	
H_2	2.0	0.98	600	3,500	
	514.6			356,700	
Heat loss through shell and rotating shaft (by difference)				16,200	4.3
				372,900	99.9

If the wet carbon is dried outside of the hearth furnace and the dried spent carbon is then baked and activated in the hearth furnace, the required heat input is 60.5% of the heat input used in the wet carbon regeneration. The calculated material and heat balance is given in Table 27. If a further step is taken and the baking is also done outside the hearth furnace, the required heat input for the hearth furnace activation is 52.4% of that required for the wet spent carbon. The calculated material and heat balance for the activation is given in Table 28.

The material and heat balance for each type of regeneration (activation) indicates the self consistency of the data and manner in which the calculations were carried out. The important information obtained from these calculations is the amount of steam-gas-air mixture input required for each type of regeneration. When converted to flue gas-steam input per pound of regenerated product, comparisons can be made with rotary tube activations.

Activating Gas Utilization

The calculated gas input per pound of regenerated product is given in Table 29 for each of the three types of hearth furnace regenerations.

TABLE 29 - ACTIVATING GAS INPUT PER POUND OF REGENERATED PRODUCT, HEARTH FURNACE

Component	Gas input, ft^3/lb		
	wet	dried	baked
N_2	27.3	16.5	14.3
CO_2	3.3	2.0	1.7
H_2O	23.7	14.3	8.6
O_2	0.75	0.45	0.36

The gas input rates for the baked carbon activation are approaching those of run 32, which are:

N_2 - 9.6 ft^3/lb
CO_2 - 1.4 "
H_2O - 5.0 "

In other operating conditions the hearth furnace activation of the baked carbon and run 32 are quite close. These are the

TABLE 27 - MATERIAL AND HEAT BALANCE, DRIED SPENT CARBON

Material	lb/hr	lb moles /hr	Temp., °F	Btu /hr	Heat, %
Input					
Spent carbon dry	116.5		70	300	0.1
Activating steam	43.3	2.38	220	3,100	21.7
ΔH_v				45,900	
Natural gas	7.8	0.432	60	000	
ΔH_c				176,000	78.1
Air for combustion	144.0			000	
	311.6			225,300	99.9
Output					
Regenerated carbon	89.4		1650	65,300	29.1
Volatile adsorbate					
ΔH_d				18,700	9.2
CO	7.4	0.26	600	1,000	
CO_2	5.1	0.12	600	700	
H_2	0.7	0.35	600	300	
Gas from activation					
ΔH_a				43,500	54.5
N_2	108.2	3.90	600	14,400	
CO_2	25.9	0.59	600	3,200	
H_2O	41.2	2.29	600	9,800	
ΔH_v				43,700	
CO	29.4	1.05	600	4,100	
H_2	2.1	1.05	600	3,700	
	309.4				
Heat loss through shell and cooling air for rotating shaft				16,200	7.2
				224,600	100.0

TABLE 28 - MATERIAL AND HEAT BALANCE, BAKED SPENT CARBON

Material	lb/hr	lb moles /hr	Temp., °F	Btu /hr	Heat, %
Input					
Baked	103.3		70	300	0.2
Activating steam	37.4	2.08	220	2,700	21.7
ΔH_v				39,600	
Natural gas	6.8	0.374	60	000	78.1
ΔH_c				152,200	
Air for combustion	124.6			000	
	272.1			194,800	100.0
Output					
Regenerated carbon	89.4		1650	65,300	33.5
Gas from activation					
ΔH_a				47,200	58.1
N_2	95.0	3.39	600	12,500	
CO_2	21.5	0.49	600	2,700	
H_2	32.9	1.83	600	7,900	
ΔH_v				34,900	
CO	30.1	1.08	600	4,200	
H_2	2.2	1.08	600	3,800	
	271.1				
Heat loss through shell and rotating shaft				16,200	8.3
				194,700	99.9

activating time and amount of carbon oxidized during the activation. The numbers are given below:

	Hearth, baked carbon	Run 32
Activating time, min	15	16
lb carbon oxidized/lb of product	0.155	0.127

In this case, the activating time is the time the carbon is at 1500°F or above. The higher value of the carbon oxidized in the hearth furnace reflects the 7% carbon loss while the particle volume decrease for run 32 is 1.9%. For run 32, the overall particle volume decrease is 2.5%.

The activating gas utilization for the three types of hearth furnace activations are:

	% utilization
wet spent carbon	17.8
dried spent carbon	29.5
baked spent carbon	43.0

For run 32, the activating gas utilization is 59.2%.

The closeness of approach of the activating conditions of the hearth furnace activation and run 32 indicates that activation of baked carbon in the hearth furnace may be feasible under conditions of rotary tube activation. Whether this will result in a decrease in carbon loss can be determined to some degree by further activation studies in the rotary tube regenerator under conditions closer to those of the hearth furnace. Whether a successful activation of baked carbon in the hearth furnace is more economical than wet carbon regeneration is a subject for economic study.

Carbon Temperature Profiles

The flame temperature, influent gas temperature and carbon temperature profiles have already been presented in Figure 6 for the regeneration of wet spent carbon. In constructing the carbon temperature curve, it was assumed that a sharp break occurs between each step. At the end of the drying step the carbon temperature is 212°F and then rises rapidly in hearth 4 to 1500°F during the baking step. From the laboratory rotary activator work, it was found that activation at temperatures below 1500°F was slow even at high activating gas throughput rates, hence; at the much shorter residence time in the multiple furnace, very little activation can be expected at temperatures below 1500°F. Above 1500°F, the activating rate becomes more rapid as the temperature rises to 1650°F, the assumed effluent temperature for the regenerated carbon.

Figure 16 shows the possible temperature profiles for the carbon and gases during regeneration of dried spent carbon. Among other assumptions, it is assumed that the vent gas is at 600°F, and the regenerated carbon leaves the 6th hearth at 1650°F. The two circles represent the calculated points. For regeneration of dried spent carbon the heat input is 60.5% of the heat input for the wet spent carbon. The gas flow through the hearths is much slower. It can be expected to give up a higher percent of its heat content to the carbon. This will bring the gas and carbon temperatures closer.

In Figure 17, where activation is the only step, the same pattern of heat exchange occurs as in Figure 16. The gas and carbon temperatures are even closer. In this case, the heat input is 52.4% of that required for the wet spent carbon.

For the latter two regenerations, the activation step has increased from 11 minutes, for the wet spent carbon, to 15 minutes. How this will affect the carbon losses is not known at present.

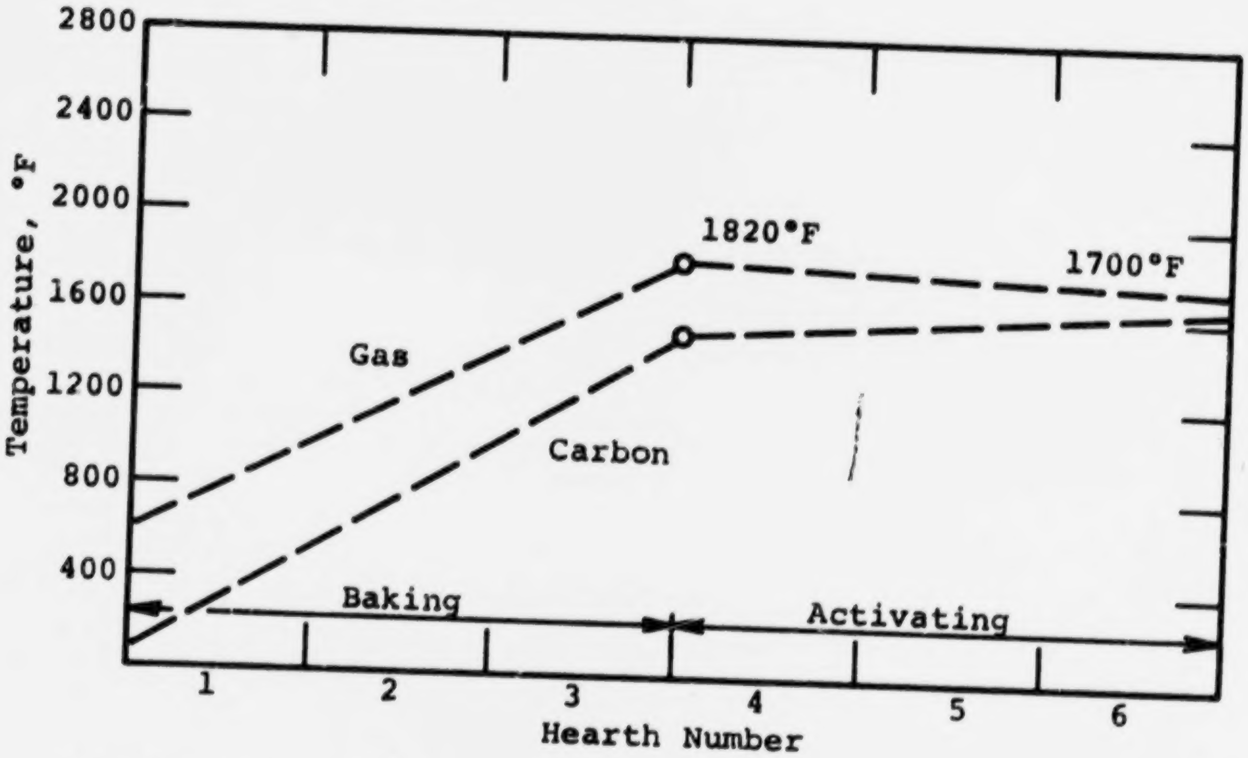


FIGURE 16 - TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE HEARTH FURNACE, REGENERATION OF DRIED SPENT CARBON

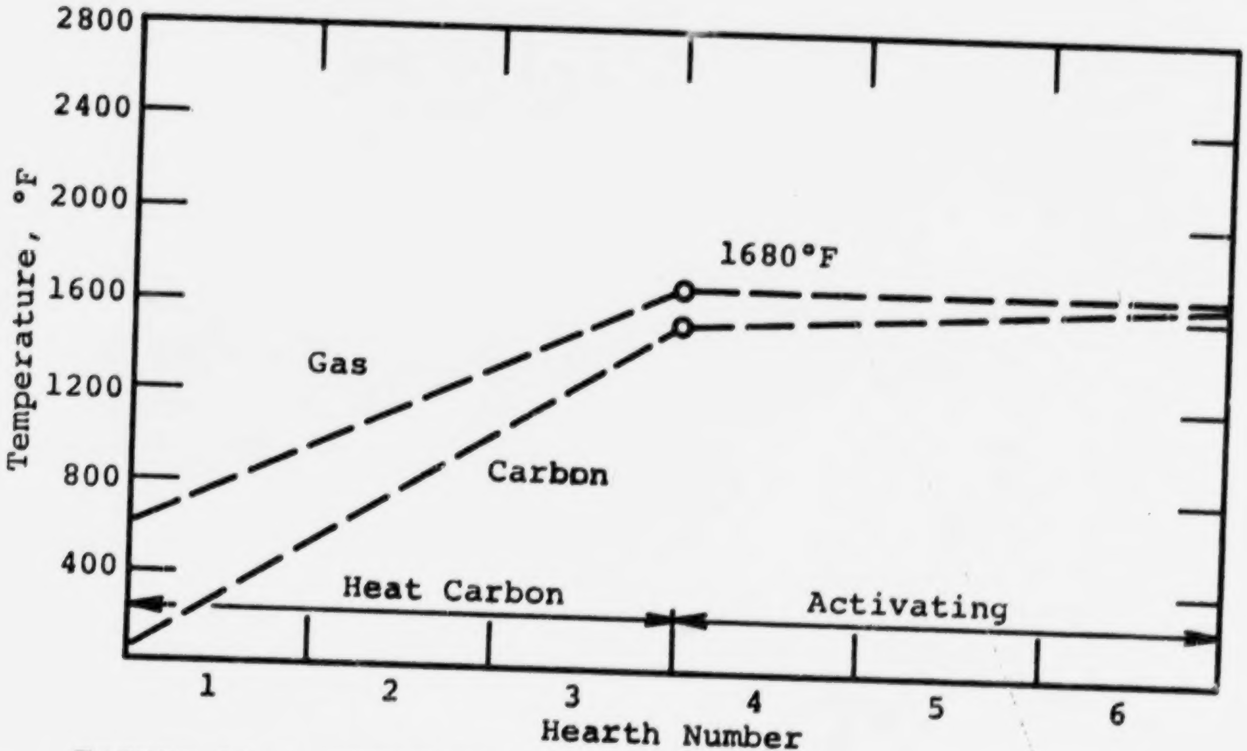


FIGURE 17 - TEMPERATURE PROFILES FOR GAS AND CARBON IN MULTIPLE HEARTH FURNACE, ACTIVATION OF BAKED SPENT CARBON

DISCUSSION AND CONCLUSIONS

The laboratory studies demonstrated a number of factors in the regeneration of granular activated carbon. Some loss of the basic carbon structure will be unavoidable since the final activation step occurs at temperatures of 1500°F and above, where carbon is readily attacked by the steam and CO_2. During attempted regenerations at temperatures below 1500°F and with high activating gas input rates, the adsorbate carbonized, evolving a volatile fraction and leaving a free carbon residue in the pores. About 60% of the adsorbate is evolved as volatiles. The remaining 40% of carbon residue oxidized very slowly at temperatures below 1500°F, hence the necessity of carrying out the final activation at 1500°F and above.

The overall regeneration of the spent carbon was found to proceed by way of three naturally occurring steps; (1) a drying step wherein the wet carbon as received from the contactors is dried, (2) a baking step wherein the adsorbate is carbonized to the volatile fraction and free carbon residue in the micropores and (3) an activating step wherein the free carbon residue is removed from the micropores by steam and CO_2 oxidation. Laboratory investigations of steps 1 and 2 have not revealed any optimum procedures that would reduce carbon losses. The success of the overall regeneration is then determined by the manner in which the activating step is performed.

In the laboratory tube regenerations, the progression of properties through the baking and activating step follow the pattern as given below for two of the spent carbons studied.

	Spent V1A		
	Dried	Baked	Activated
Bulk density, g/cc	0.616	0.546	0.493
Particle density, g/cc	0.990	0.876	0.789
Real density, g/cc	1.88	2.13	2.15
Pore volume, cc/cc particle volume	0.473	0.590	0.633
Iodine number	529	798	886
Molasses number	172	198	249

	Once-Spent Filtrasorb 400		
	Dried	Baked	Activated
Bulk density, g/cc	0.584	0.532	0.502
Particle density, g/cc	0.971	0.871	0.825
Real density, g/cc	1.88	2.07	2.13
Pore volume, cc/cc particle volume	0.484	0.578	0.613
Iodine number	673	955	1017
Molasses number	174	193	192

The properties of the activated once-spent Filtrasorb 400 essentially fall into the property ranges of the virgin Filtrasorb 400, indicating a good recovery of all the essential properties. Attempts to bring the iodine number of spent V1A to the 1000 level have all failed. It was finally concluded that, at the Pomona plant, this particular carbon quantity which was sent to MSAR had been activated in a manner to change the physical properties of the basic carbon.

A particle volume decrease has been observed during the baking step although the baking atmosphere is nonoxidative. Furthermore, the baking temperatures are sufficiently low to rule out oxidation by water vapor or CO_2 released from the adsorbate. The investigations which have attempted to attribute the particle volume decrease to carbon shrinkage and/or removal of sewage residue on the outer surfaces of the carbon particles have not been conclusive. The results, however, appear to favor the sewage residue concept. The estimated particle volume decrease, by either shrinkage and/or sewage residue removal, is about 1.0% of the 1.3% average measured on about 20 baked carbons.

Carbon loss can show up on the first reactivation when the activating conditions are sufficiently severe to cause decrease in particle size, i.e., external burnoff. It can show up on later reactivations if most of the basic structure burnoff is internal. By internal burnoff, the pore walls thin out making the exterior layers of the carbon less resistant to abrasions. Even on normal handling, the carbon particles break down forming fines of less than 40 mesh. These fines being back washed out of the contactors measure up as carbon loss.

Multiple-hearth furnace reactivations, as performed at the Pomona plant, have suffered an average carbon loss of 7% as measured by bulk volume decrease in the contactors. In the laboratory work, conditions have been found by which once-spent Filtrasorb 400 has been regenerated to virgin carbon properties with overall particle volume decreases of 2.8% and 2.9% on two regeneration runs. In these runs the particle volumes decreased during baking by 1.3% and 0.9%, respectively. When allowances are made for the possible baking shrinkage and residue removal, the particle volume decreases that represent true carbon losses are then 1.8% and 2.0%. Sieve analyses of activated products show 0.15% of -40 mesh fines. When this loss is added to the above particle volume decreases the best measured carbon losses on these two runs are 1.9% and 2.1%. Spent V1A carbon has repeatedly been regenerated to the virgin carbon bulk density level but the virgin carbon adsorptive properties were not recovered. For this carbon, the overall mean particle volume decrease for 19 regenerations was 2.9%. When the baking and fines corrections are applied the mean carbon loss is 1.3%.

The large difference in carbon loss between the multiple hearth furnace and the rotary tube regenerator appears to be due to the different activating conditions. In the hearth-furnace regeneration of wet spent carbon, the furnace functions as a dryer, baker and activator. Since the heating requirement cannot be separated from the activating gas requirement, the large heating load due to the drying and also baking requires an excess of heating gas relative to the activating step. The hearth furnace activation is characterized by a large activating gas input rate, a short activating time, low activating gas utilization rate and relatively low carbon temperatures. In the rotary tube regenerator, where the activating gas input rate can be regulated independently of heat requirements, the activation is characterized by low gas input rate, slightly longer activating time, higher activating gas utilization rate and higher carbon temperatures. In both activations the gas temperatures were at the 1700°F level. The operating data on the hearth furnace and two laboratory runs show this difference:

	Run 32	Run 36	Hearth Furnace
N_2 std ft^3/lb	9.6	7.4	27.3
CO_2 std ft^3/lb	1.4	1.0	3.3
H_2O std ft^3/lb	5.0	1.9	23.5
O_2 std ft^3/lb	0.0	0.0	0.7
Carbon temperature,°F	1630	1630	1570
Activating time, min	16	16	11
Gas utilization, %	59	66	18

Further laboratory work is required wherein the hearth furnace activating conditions are closely duplicated to determine whether the above stated operating conditions are the real cause of the higher carbon losses. By performing the drying and baking steps separately, the calculated gas input rate for a hearth furnace activation comes much closer to the optimum rates used in the rotary tube. The degree of effectiveness of this change can also be determined with the laboratory regenerator.

Vent gas analysis as a means for monitoring the activation has shown promise but considerable difficulties have been experienced in getting consistent results.

Carbon quenching experiments have shown some decrease in iodine number but not as large as reported at the Pomona plant. No correlation with pore structure or molasses number was observed.

It appears now quite feasible to perform the drying and baking steps in a multiple hearth furnace by adjusting the operating conditions so that the carbon temperature never exceeds 1500°F and that the carbon discharge temperature is 1500°F. On the second pass through the hearth furnace the carbon is brought up to the activating temperature with gas input rate near that given in Table 29.

RECOMMENDATIONS

Work in several areas of the spent carbon regeneration field are recommended on the basis of the funding of this program. These recommendations are listed as follows:

1. Study of Activating Parameters

In deciding the best method of regeneration that should be used, it is essential that the exact cause of the hearth furnace regeneration losses be determined. Work done so far indicates that it is due to the high gas through-put rate. By duplication of the hearth furnace conditions this can be verified.

Parameter studies to establish operating limits are required for engineering of the process and equipment and to subsequently determine the relative economics of regeneration by (1) indirect heated rotary tube furnace, (2) direct fired multiple hearth furnace,(3) a combination of the two and (4) a two pass regeneration using the multiple hearth furnace.

2. Adsorption-Regeneration Cycle Studies

It can be expected with a fair degree of certainty that, on each regeneration, some damage will occur to the pore structure even under the optimum regenerating conditions. For the economic evaluation, it is essential to determine the extent of this damage. This study requires the performance of successive adsorption-regeneration cycles, starting with virgin carbon, and evaluating the product on each regeneration.

3. Determination of Feasibility of Low Grade Carbon as Make Up

Damage to carbon structure manifests itself as reduced abrasion resistance and consequent fines losses. A lower activity carbon has further to go before it comes friable, hence, cheaper lower grades may present an economic advantage.

4. Chemical Oxidation

Treatment of spent carbon with a chemical oxidant such as hydrogen peroxide is known to remove some of the adsorbate. In conjunction with the baking step, this procedure may lower the carbon residue in the micropores. The smaller carbon residue will require less severe activating conditions and thus reduce carbon loss.

APPENDIX A$^{(5)}$

IODINE NUMBER

The Iodine Number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine concentration of the residual filtrate is 0.02 normal.

Procedure

1. Grind a representative sample of carbon until 90% or more will pass a 325-mesh sieve (by wet screen analysis).
2. Dry the sample for a minimum of three hours in an electric drying oven maintained at 150°C.
3. Weigh 1.000 gram of dried pulverized carbon (see note 2).
4. Transfer the weighed sample into a dry, glass-stoppered, 250-ml Erlenmeyer flask.
5. To the flask add 10 ml of 5%-wt HCl acid and swirl until carbon is wetted.
6. Place flask on hotplate, bring contents to boil and allow to boil for only 30 seconds.
7. After allowing flask and contents to cool to room temperature, add 100 ml of standardized 0.1 normal iodine solution to the flask.
8. Immediately stopper flask and shake contents vigorously for 30 seconds.
9. Filter by gravity immediately after the 30-second shaking period through an E & D folded filter paper.
10. Discard the first 20 or 30 ml of filtrate and collect the remainder in a clean beaker. Do not wash the residue on the filter paper.
11. Mix the filtrate in the beaker with a stirring rod and pipette 50 ml of the filtrate into a 250 ml Erlenmeyer flask.
12. Titrate the 50 ml sample with standardized 0.1 normal sodium thiosulfate solution until the yellow color has almost disappeared.

13. Add about 2 ml of starch solution and continue titration until the blue indicator color just disappears.

14. Record the volume of sodium thiosulfate solution used.

15. Calculate the Iodine Number as follows:

$$\frac{X}{m} = \frac{A - (2.2B \times \text{ml of thiosulfate solution used})}{\text{weight of sample (grams)}}$$

$$C = \frac{N_2 \times \text{ml of thiosulfate solution used}}{50}$$

$$\text{Iodine Number} = \frac{X}{m} D$$

X/m = mg iodine adsorbed per gram of carbon
N_1 = normality of iodine solution
N_2 = normality of sodium thiosulfate solution
A = $N_1 \times 12693.0$
B = $N_2 \times 126.93$
C = residual filtrate normality
D = correction factor (obtained from attached graph)

Notes on Method

1. The capacity of a carbon for any adsorbate is dependent on the concentration of the adsorbate in the medium contacting the carbon. Thus, the concentration of the residual filtrate must be specified, or known, so that appropriate factors may be applied to correct the concentration to agree with the definition.

2. The amount of sample to be used in the determination is governed by the activity of the carbon. If the residual filtrate normality (C) is not within the range 0.008N to 0.035N, given on the Iodine Correction Curve, the procedure should be repeated using a different size sample.

3. It is important to the accuracy of the test that the potassium iodide to iodine weight ratio is 1.5 to 1 in the standard iodine solution.

Reagents and Equipment

Hydrochloric acid, 5% wt - To 550 ml of distilled water add 70 ml of reagent-grade concentrated hydrochloric acid.

Sodium Thiosulfate, 0.1 normal - In a one-liter volumetric flask dissolve 24.82 grams of reagent-grade sodium thiosulfate crystals ($Na_2S_2O_3 \cdot 5H_2O$) in distilled water. Add about 0.1 gram of reagent-grade sodium carbonate and dilute to the one-liter mark. This solution should be allowed to stand for a few days before standardizing.

Standardize with reagent-grade metallic copper. Dissolve about 0.2 grams of copper, weighed to the nearest 0.1 mg, in 5 ml of concentrated nitric acid and boil gently to expel brown fumes. Dilute to about 20 ml with distilled water and add ammonia water dropwise until the solution is a deep blue color. Boil again until the odor of the ammonia is faint. Neutralize with acetic acid until the precipitate which forms with the acid dissolves and add 5 or 6 drops in excess. Again bring to boiling. Cool to room temperature. Add solid potassium iodide in sufficient amount to redissolve the copper iodide precipitate which forms. Titrate with sodium thiosulfate until the iodine fades to a light yellow color. Add starch indicator and continue the titration by adding the thiosulfate dropwise until a drop produces a colorless solution. Calculate the normality of the sodium thiosulfate as follows:

$$\text{Normality of sodium thiosulfate} = \frac{\text{weight copper}}{\text{ml thiosulfate} \times 0.06354}$$

Iodine Solution - Dissolve 127 grams of reagent-grade iodine and 191 grams of potassium iodide in distilled water. (See Note 3). Dilute to one liter in a volumetric flask. To standardize the iodine solution, pipette 25.0 ml into a 250 ml Erlenmeyer flask and titrate with the standardized 0.1N sodium thiosulfate. Use the starch indicator when the iodine fades to a light yellow color. Then finish the titration by adding the thiosulfate dropwise until a drop produces a colorless solution.

Calculate the normality of the iodine solution as follows:

$$\text{Normality of iodine solution} = \frac{\text{ml thiosulfate x normality thiosulfate}}{25}$$

Starch Indicator - Mix one gram of soluble starch with a few ml of cold water. Pour the mixture into one liter of boiling water and allow boiling to continue for a few minutes. This solution should be made up fresh daily for best results.

Filter Paper - E & D, folded filter paper, 18.5 cm, No. 192. Burrell Corporation Catalog No. 34-390.

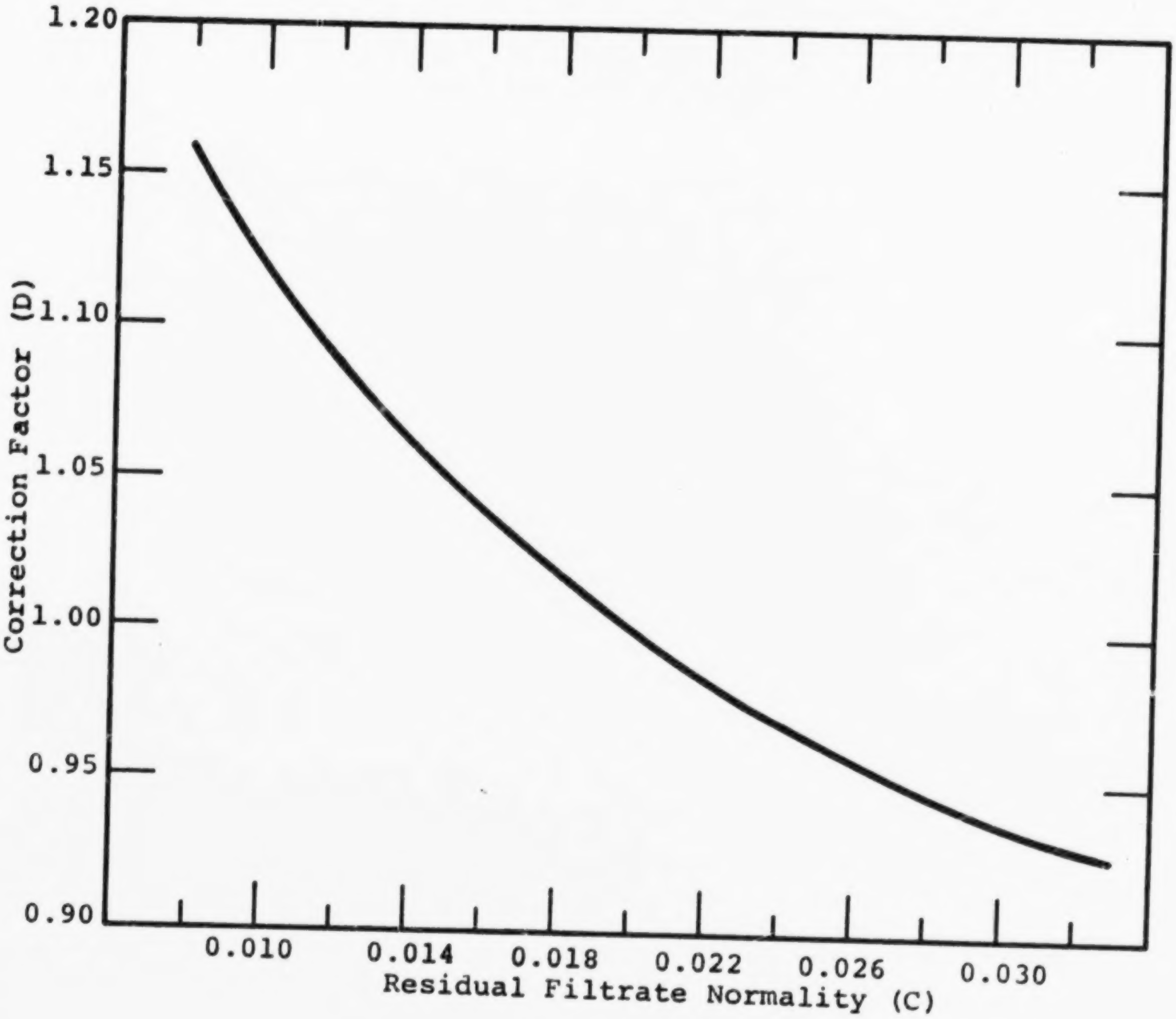


FIGURE 18 - IODINE CORRECTION CURVE

APPENDIX B(5)

MOLASSES NUMBER

Molasses solutions are treated with pulverized activated carbon of unknown decolorizing capacity and with a standard carbon of known Molasses Number. The optical densities of the filtrates are measured and the Molasses Number of the unknown is calculated from the ratio of the optical densities and the standard value.

Procedure

1. Grind a representative sample of carbon until 90% or more will pass a 325-mesh screen (by wet screen analysis).
2. Weigh 0.46 gram portions of pulverized standard carbon of known decolorizing capacity and unknown carbon and transfer to separate 400 ml beakers.
3. Add 50.0 ml of molasses solution to each beaker and stir until the carbon is thoroughly wetted.
4. Place the beakers on hotplate and allow to boil for 30 seconds.
5. Immediately after boiling filter the samples by vacuum through a Buchner funnel, using Whatman No. 3 filter paper which has been previously coated by filtering 50 ml of the filter paper suspension (see Note 2). Discard the first 10 to 15 ml of the sample filtrate and collect remainder.
6. Using a 2.5 mm effective light path and a 425 mu (blue) filter, compare the optical densities of the samples against distilled water in a Fisher Electrophotometer or other suitable instrument (see Note 3).
7. Calculate the Molasses Value as follows:

$$\text{Molasses Value} = \frac{K \times b}{A}$$

K = Molasses value of standard carbon
A = Optical density of filtrate from carbon being tested
b = Optical density of filtrate from standard carbon

Notes on Method

1. Any grade of commercial molasses which may be purchased will vary considerably in depth of color. The dilution of the initial solution to give the same final filtrate color with the standard carbon compensates for such variations. Once such an adjustment has been made on a given lot of molasses, the proper dilution may be made routinely.
2. The Buchner funnels and precoated filter paper should be prepared beforehand so that no delay is encountered in filtering the samples. Discard the filtrate from the filter paper suspension before filtering the samples.
3. Since the Fisher Electrophotometer is not equipped with 2.5 mm-cells, the cell holder was modified to accommodate the 10-mm Klett Summerson cell. A 2.5-mm effective light path is obtained by placing in the 10-mm cell a 7.5-mm glass immersion plate.

Reagents and Equipment

Standard carbon - Small quantities of primary standard carbon are available from the Activated Carbon Division, Pittsburgh Coke & Chemical Company.

Molasses solution - Prepare by diluting 146 grams (see Note 1) of blackstrap molasses with one liter of distilled water. The weight of molasses to be used varies with the particular lot of molasses and is adjusted, if necessary, so that the standard carbon produces a filtrate with an optical density of 0.38 to 0.42. The molasses solution is stored in a refrigerator and any unused portion discarded after 24 hours. A suitable grade of Plantation blackstrap molasses can be obtained at any local health food store.

Filter paper suspension - Prepare by mascerating 16 circles of Whatman No. 3, 7-cm filter paper in one liter of distilled water.

Absorption cell - Klett Summerson, No. 902, 10-mm.

Immersion plate - Klett Summerson, No. 903, 7.5-mm.

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4. Communication from Arthur N. Masse, FWPCA Water Research Laboratory, Cincinnati to Charles W. Carry, Los Angeles County Sanitary District on observations made by Carl Brunner, January 11, 1968.
5. Iodine and molasses decolorizing tests are standard tests used in the activated carbon industry to determine activity of liquid phase carbons. Origin of these test procedures was not available.